PB170 741

ENVIRONMENTAL HEALTH SERIES
Water Supply
and Pollution Control

EVALUATION OF VARIOUS ADSORBENTS AND COAGULANTS FOR WASTE-WATER RENOVATION

AWTR-12

Pgs: 61, $75

CLEARINGHOUSE
FOR FEDERAL SCIENTIFIC AND
TECHNICAL INFORMATION

Hardcopy	Microfiche		
$ 3.00	$ 0.75	58 pp	

ARCHIVE COPY

U. S. DEPARTMENT OF HEALTH
EDUCATION, AND WELFARE

Public Health Service

Advanced Waste Treatment Research Publications

Although over-all guidance of AWTR research projects is provided by the AWTR Program, the results obtained, opinions expressed, and conclusions reached by the contractors are their own and are not necessarily endorsed by the Department of Health, Education, and Welfare. Except for editorial review and abridgments as necessary, these reports appear as received from the contractors.

	Report Number
AWTR-1 Summary Report, June 1960 - December 1961	W62-9
AWTR-2 Preliminary Appraisal of Advanced Waste Treatment Processes	W62-24
AWTR-3 Ultimate Disposal of Advanced Treatment Wastes	999-WP-3
Part 1. Wet Oxidation	
Part 2. Incineration	
AWTR-4 Waste-Water Renovation	999-WP-4
Part 1. A Design Study of Freezing and Gas Hydrate Formation	
Part 2. Feasibility Tests of Freezing	
AWTR-5 Contaminant Removal from Sewage Plant Effluents by Foaming	999-WP-5
AWTR-6 Cost of Purifying Municipal Waste Waters by Distillation	999-WP-6
AWTR-7 Advanced Waste Treatment by Distillation	999-WP-9

(Continued on inside back cover.)

(Continued from inside front cover.)

		Report Number
AWTR- 8	Ultimate Disposal of Advanced-Treatment Waste	999-WP-10
	Part 1. Injection	
	Part 2. Placement in Underground Cavities	
	Part 3. Spreading	
AWTR- 9	Adsorption of Biochemically Resistant Materials from Solution	999-WP-11
AWTR-10	Feasibility of Granular, Activated-Carbon Adsorption for Waste-Water Renovation	999-WP-12
AWTR-11	Evaluation of the Use of Activated Carbon and Chemical Regenerants in Treatment of Waste Water	999-WP-13

EVALUATION OF VARIOUS ADSORBENTS AND COAGULANTS FOR WASTE-WATER RENOVATION

by

J. N. Williamson,
A. H. Heit,
and C. Calmon

for

The Advanced Waste Treatment Research Program
Basic and Applied Sciences Branch
Robert A. Taft Sanitary Engineering Center

A report submitted in fulfillment of a contract between the Public Health Service and Ionac Chemical Co. (Contract No. PH 86-62-29). Submitted December 1962.

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Division of Water Supply and Pollution Control

June 1964

The ENVIRONMENTAL HEALTH SERIES of reports was established to report the results of scientific and engineering studies of man's environment: The community, whether urban, suburban, or rural, where he lives, works, and plays; the air, water, and earth he uses and re-uses; and the wastes he produces and must dispose of in a way that preserves these natural resources. This SERIES of reports provides for professional users a central source of information on the intramural research activities of Divisions and Centers within the Public Health Service, and on their cooperative activities with State and local agencies, research institutions, and industrial organizations. The general subject area of each report is indicated by the two letters that appear in the publication number; the indicators are

WP - Water Supply
and Pollution Control
AP - Air Pollution
AH - Arctic Health
EE - Environmental Engineering
FP - Food Protection
OH - Occupational Health
RH - Radiological Health

Triplicate tear-out abstract cards are provided with reports in the SERIES to facilitate information retrieval. Space is provided on the cards for the user's accession number and additional key words.

Public Health Service Publication No. 999-WP-14

ADVANCED WASTE TREATMENT RESEARCH PROGRAM

The Advanced Waste Treatment Research Program of the Public Health Service has two ultimate goals: One is to help abate our Nation's growing water pollution problems, and the other, more startling in concept, is to renovate waste water for direct and deliberate re-use.

Conventional water and waste treatment practices have little or no effect on many simple inorganic salts and permit an ever-increasing number and amount of highly complex, synthetic organic wastes to contaminate drinking water supplies. If we are to protect these water supplies for the future, it is mandatory that new technologies for water and waste treatment be developed.

Advanced Waste Treatment may be looked upon as a two-step process: (1) Separating concentrated contaminants from the purified water "product," and (2) disposing of the concentrated contaminants in a way that will render them forever innocuous. This "permanent disposal" of separated wastes is essential so that useable surface or ground waters will not be contaminated and so that the same contaminants need not be removed again and again from water supplies.

In one step, then, advanced waste treatment, i.e., water renovation, could alleviate both water pollution and water supply problems -- problems of increasing concern both in this country and in the rest of the world. The importance of advanced waste treatment was recognized by Congress in its 1961 amendments to the Federal Water Pollution Control Act (Public Law 87-88). This act directs the Secretary of Health, Education, and Welfare ". . . to develop and demonstrate practicable means of treating municipal sewage and other water-borne wastes to remove the maximum possible amounts of physical, chemical, and biological pollutants in order to restore and maintain the maximum amount of the Nation's water at a quality suitable for re-use.

It is too early to predict accurately the cost of advanced waste treatment technology, but the need is inevitable. Because of population increase and industrial expansion, we are approaching the time when our rivers and streams will no longer be able to assimilate our wastes and when there will be no more developable supplies of fresh water. Whatever the cost of this technology, one thing is certain -- it must be the very lowest science and engineering can achieve. Anything more will impose an inexcusable, perhaps intolerable burden on our country's economic growth and on its ability to compete in tomorrow's world.

The Ionac Chemical Company, a division of Pfaudler-Permutit Inc., was formed to deal with the chemical and physical aspects of water and waste-water treatment. The removal of organic impurities from water has been of interest to them because of the fouling of ion exchange beds. They have developed special activated carbons and decolorizing resins for removing these organics. Dr. Calmon, Mr. Heit, and Mr. Williamson, the authors of this report, have been closely associated with this work and are, therefore, particularly qualified for working on this contract.

The writers gratefully acknowledge the assistance of the following commercial concerns and institutes in the furnishing of samples and technical information used in this study:

Great Lakes Carbon Corporation
General Reduction Company
Berkshire Chemical Company
American Vermiculite Corporation
Swift and Company
American Potash and Chemical Corp., Lindsay Chemical Division
Charles A. Wagner Co., Inc.
National Lead Company, Titanium Alloy Manufacturing Division
Miles Chemical Company, Division of Miles Laboratories, Inc.
Archer-Daniels-Midland Company
Georgia-Pacific Chemical Company
Georgia Kaolin Company
Minerals and Chemicals Phillip Corporation
Hercules Powder Company
Shell Chemical Company, Division of Shell Oil Company
California Products Corporation
Metal and Thermit Corporation
Floridin Company
Corn Products Company
John R. Borst, Inc.
National Casein of New Jersey
American Cyanamid Co.
American Colloid Co.
Pittsburgh Plate Glass Company, Chemical Division
West Virginia Pulp and Paper Co.
Johns-Manville
Arizona Minerals Corporation
The Soap and Detergent Association

The writers gratefully acknowledge the assistance so freely given by the following persons in providing samples of secondary effluents:

Mr. J. W. Goodfellow, in charge of operations at the Mt. Holly Sewage Plant, Mt. Holly, N.J.

Mr. J. Frazee and Mr. J. Drew, in charge of operations at the 32d and Farragut Sewage Treatment Plant, Camden, N.J.

A special acknowledgment is also given to Dr. A.H. Greer and his staff, Polymers Research Section and Mr. J. Ungar, Manager of Technical Service (of Ionac Chemical Company) for use of personal papers and samples of experimental polymer formulations.

CONTENTS

	Page
ABSTRACT	vii
INTRODUCTION	1
Background	1
Object of This Investigation	2
Approach Used	2
Literature Survey	3
Effluent Waters Used	3
Waste-Water Effluents	3
Synthetic Laundromat Effluent	3
Rancocas Creek Water	4
Effluent Treatments	5
TECHNICAL DISCUSSION	6
Nature of Materials To Be Removed	6
Mechanisms of Removal Amenable to the Sludge Blanket Process	7
Adsorption and Ion Exchange	7
Coagulation	8
Oxidation	8
Materials and Formulations Tested via Batch, Columnar Bed, and Sludge Blanket Treatments	8
Adsorbents in Batch Testing	8
Coagulants and Coagulant Aids in Batch Testing	10
Oxidants and Oxygen Transfer Agents in Batch Tests	10
Combination Batch Treatments	10
Columnar-Bed Testing	10
Sludge Blanket Testing	11
METHODS AND RESULTS	11
General	11
Batch Testing of Adsorbents	13
Synthetic Laundromat Effluent	13
Unfiltered Secondary Effluent	15
Secondary Effluent Prefiltered Through Whatman No.5 Paper	16
Sodium Bisulfite-Treated Wood	25
Sodium Hypochlorite- and Ammonia-Treated Wood	25
Batch Testing of Coagulants and Coagulant Aids	26
General Procedure	26
Organic Materials	26
Inorganic Materials	37
Batch Testing of Oxidants and Oxygen Transfer Agents	39
Batch Testing of Combinations of Materials	40

Columnar-Bed Testing 41
Ion Exchange Resins 43
Ionac A-300 and Ionac A-540 43
Ionac A-260 44
Ionac XLA-400. 45
Resin bed No. 1 45
Resin bed No. 2 45
Ionac XLA-400 resin (chloride form), 95-milliliter bed 45
Ionac C-270 and C-240 (H^+ forms). 47
Proteinaceous Materials 47
Forty Percent Gluten Feed Supplement 48
Casein and Soya Protein 48
Modified Proteinaceous Materials 48
Reaction of Dispersed Proteins With Ferric Compounds 49
Reaction of Undispersed Proteins With Ferric Compounds 50
Reaction of Proteins With Formaldehyde 50
Reaction of Undispersed and Dispersed Protein With Formaldehyde plus Various Other Compounds 52
Inorganic and Treated Inorganic Materials 58
Calcined, Diatomaceous Earth 58
Inorganic Materials Treated with Rosin Amine D Acetate. 58
Activated Carbon 58
Sludge Blanket Testing 59
Regeneration and Cost Estimate Studies 62
Cost Studies: Solid Adsorbents, Coagulants 62
Cost Studies: Bed Materials 64
DISCUSSION AND CONCLUSIONS 66
Adsorbents 66
Coagulants 67
Costs 67
RECOMMENDATIONS 68
REFERENCES 71
SELECTED READINGS 73
APPENDIX A: U.S. Patent 2,393,269 87

ABSTRACT

An investigation was undertaken to learn whether cheap, commercially available materials hold promise in the treatment of waste waters, especially secondary effluents. Minerals, industrial by-products, proteinaceous materials, conventional water treatment agents, and others were tested. Activated carbon was used as a reference.

Some minerals exhibit minor affinities for the organic-solute phase of secondary waste-water effluents. Minerals treated with salts of tetravalent metals show promise for this purpose. Most conventional coagulants exhibit marked affinities for the refractory organic materials in secondary waste-water effluents. Proteins evidence similar properties when coagulated in the presence of mineral acids and certain acid salts of trivalent metals. Hydrophobic proteins, aldehyde-hardened in granular shape then further reacted with acids or acid salts, will also remove organic refractory contaminants from secondary effluents. These materials can be used in bed form and are regenerable. Organic anion exchangers will also remove organic solutes from waste water. The problem of irreversible organic fouling requires more attention if exchangers are to be considered in advanced waste treatment. Precoagulation of the higher molecular species of organics is suggested as a fouling preventive measure.

This study demonstrated the feasibility, at least from a mechanical standpoint, of incorporating solid adsorbents into the sludge blanket process for water treatment in the presence or absence of coagulants. The sludge blanket process can combine the virtues of the finely divided, large-surface-area forms of solids and flocs (normally associated with batch treatment techniques or vacuum filtrations) with the maintenance of relatively high flow rates, normally associated with columnar-bed techniques. Material cost factors are discussed for the various materials tested and for the treatments involving their use. Recommendations are made for possible further lines of investigation.

BLANK PAGE

EVALUATION OF VARIOUS ADSORBENTS AND COAGULANTS FOR WASTE-WATER RENOVATION

Introduction

Background

Present-day waste-water treatments result in secondary effluents, which are discharged into receiving streams, rivers, or bays, and in sludges, which are burned or spread on the soil. The secondary effluents invariably contain small amounts of materials that have resisted efforts to degrade or otherwise render them innocuous. Accordingly, these materials, termed "refractory," build up in waters as the waters are used and re-used.

As the population increases, the water supply can only remain relatively constant. Coastal areas and areas with nearby bodies of brackish water are beginning to turn to the purifying of high-salinity water to increase their water supplies. In general, however, all areas are now faced with the need for more and more water re-use and with the problems resulting therefrom. Increases in (a) production of domestic, industrial, and agricultural wastes; (b) synthesis and use of difficultly degradable (or undegradable) organic compounds; and (c) water consumption are compounding these problems with a resultant buildup of refractory contaminants in water supplies.

To combat the problems posed by refractory contaminants, biologically degradable materials can in some cases be substituted into common usage for difficultly degradable materials. In many cases, however, this would be a backward step. The most probable ultimate solution of the refractory-contaminant-removal problem would appear to lie in the direction of more advanced measures for water and waste-water treatment.

Many studies on the removal of refractory contaminants from waters have been or are being undertaken. These studies include use of techniques such as ion exchange, adsorption, coagulation, oxidation, electrodialysis, electrolysis, foam fractionation, and distillation. The ultimate goal of all this

work is a process (or combination of processes) whereby direct re-use of water, with no natural body of water serving as an intermediate carrier, can be made commonplace.

Object of This Investigation

This investigation was undertaken to learn:

(a) Whether any cheap, commercially available materials (such as, but not limited to, industrial by-products or scrap, or naturally occurring minerals, clays, earths, and the like) possess the capability of adsorbing, or otherwise removing, the refractory contaminants in waters that have been re-used, especially domestic secondary effluents; and

(b) whether these materials, if proved useful for this purpose, might be best utilized in a sludge blanket process.

The sludge blanket process is considered a likely technique for taking advantage of any adsorptive or ion exchange properties of cheap, solid materials, since these properties would no doubt be best exhibited in the finely divided state. A columnar bed, for example, would have to consist of larger particles with a smaller surface-area-to-bed-volume ratio to get an adequate flow rate.

This study was not limited to solid materials, of course; it also included materials in liquid or gaseous form, or in solution. The main criterion stressed was massive refractory-contaminant removal at comparatively low cost. Accordingly, coagulation and oxidation were integral parts of these experiments.

Approach Used

Throughout this study primary emphasis was placed on removal of organic refractory contaminants, as evidenced by the dichromate reduction method for determination of chemical oxygen demand (COD). Chloride and other inorganic ions were recognized as refractory contaminants. Accordingly, tests were conducted to determine if any inorganic contaminants were being removed in the course of each treatment tested. Frequently, substitution of inorganic for organic materials was considered when it was known that the inorganic materials thus imparted into the water could be removed at a very low cost for additional treatment. In addition to the COD test, testing procedures included analyses for chloride ion, dissolved solids, total solids, alkylbenzenesulfonate detergents (ABS), and pH.

Testing procedures were in accordance with Standard Methods for the Examination of Water and Waste Water, Eleventh Edition, 1960.

LITERATURE SURVEY

The first step in this project was to survey the literature. Pertinent references to treatment and re-use of waters, especially of waste waters, were noted and recorded. Of special interest, of course, were references to materials that would be amenable to the sludge blanket process. Emphasis was therefore placed on topics such as adsorption, ion exchange, coagulation, and oxidation, with less attention to references concerning topics such as electrodialysis, electrolysis, and foam fractionation.

EFFLUENT WATERS USED

Waste-Water Effluents

The waste-water effluent used in these experiments was secondary waste-water effluent, largely of domestic origin, but with a few small industries contributing to it. It was obtained from the Mt. Holly, N. J., Sewage Plant. Owing to the limited size of the receiving stream, (the Rancocas Creek) the treatment facilities in this plant include chlorination to control pathogens. Cross-checks of testing procedures were occasionally run with effluent obtained from the 32d and Farragut Streets Sewage Plant in Camden, N. J. No chlorination step is included in the production of this Camden waste-water effluent, which is discharged into the Delaware River. For the most part the effluent was filtered (via a vacuum filtration using Whatman No. 5 paper) prior to experimental treatment.

Flow diagrams of the waste-water treatment plants are depicted in Figures 1 and 2.

Synthetic Laundromat Effluent

To investigate the effect of some materials on ABS, tests were conducted with a synthetic laundromat effluent. This was done to approximate the conditions under which ABS is associated with other compounds and materials in some trade effluents. This synthetic laundromat effluent contained the following: 60 ppm standard ABS (100% basis), 200 ppm Na_3PO_4, 4 ppm NaOCl, 5 ppm sodium carboxy methyl cellulose, 5 ppm urea, 5 ppm $(NH_4)_2CO_3$, 100 ppm $CaCl_2$, 30 ppm $MgSO_4$, and 50 ppm NaCl.

Rancocas Creek Water

In one instance, the highly colored water of the Rancocas Creek at Birmingham, N.J., was employed to test an adsorbent. This liquor was prefiltered through Whatman No. 5 paper. The

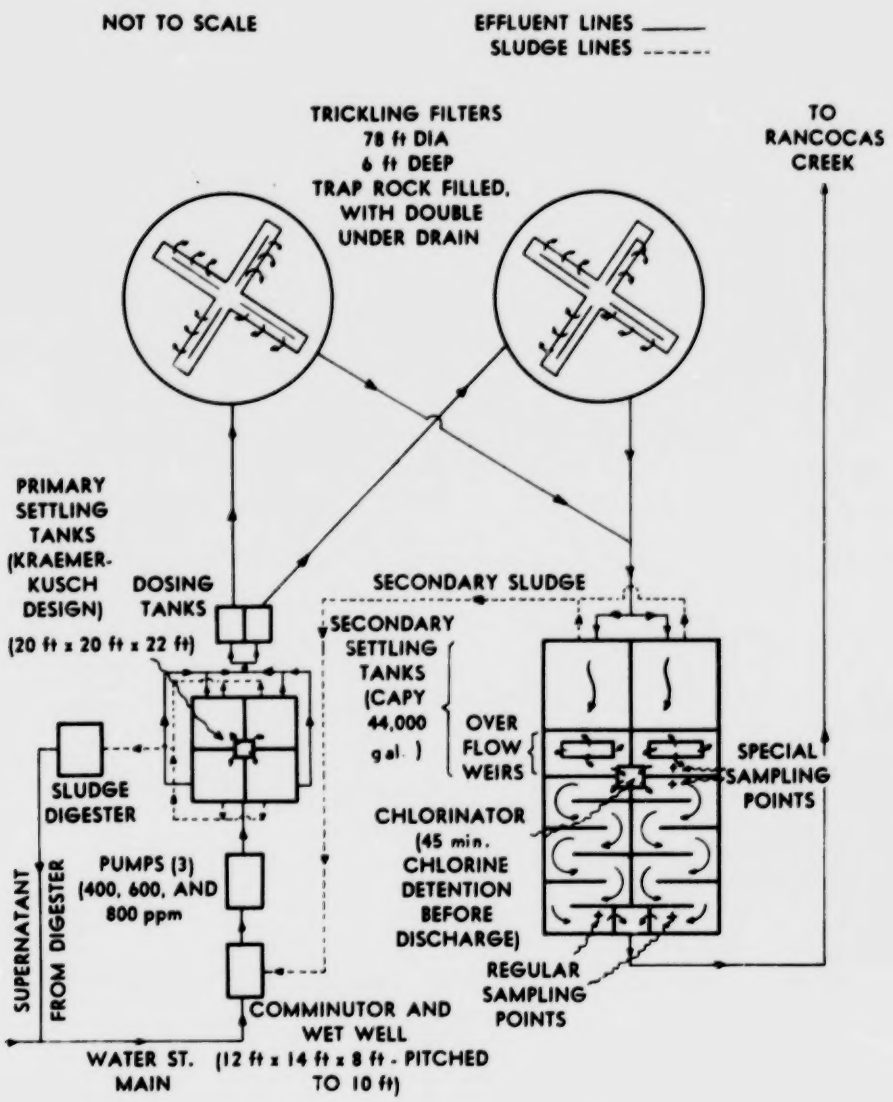


Figure 1. Mt. Holly, N.J., sewage treatment plant (trickling filter process).

purpose here was to note the affinity of the adsorbent for the color bodies (largely humates and humic acids) in the water. The authors believe that high-molecular-weight acids and their salts, similar to (and possibly in some cases identical to) humic acids

and humates, account for a major portion of the organic refractory contaminants in secondary waste-water effluents. [1, 2, 3]

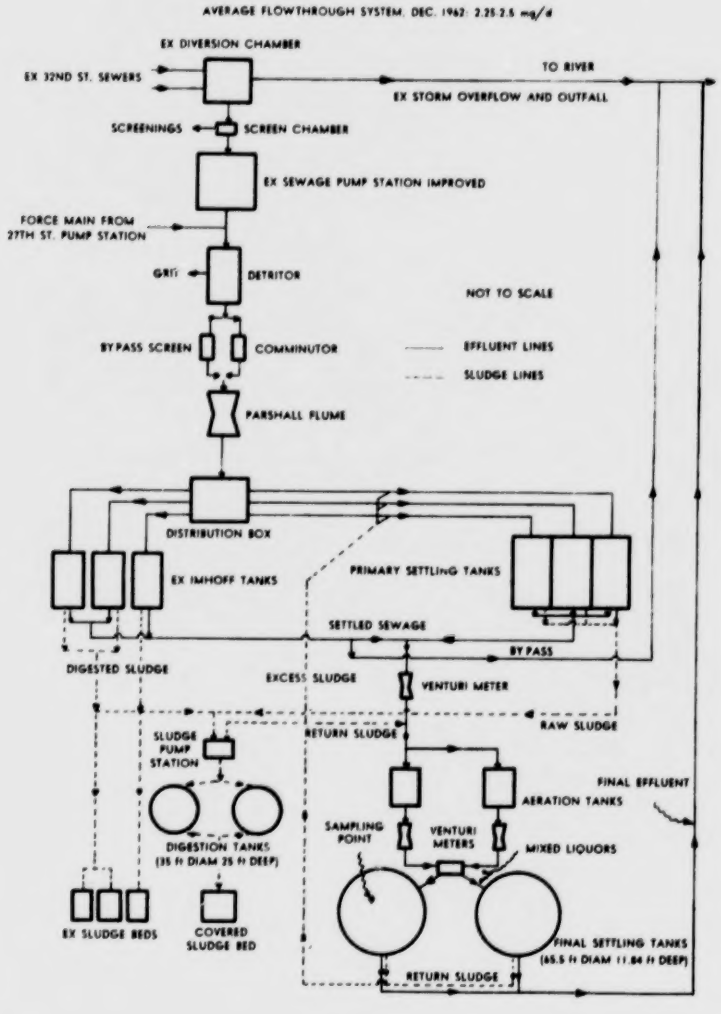


Figure 2. Flow diagram, 32d St. and Farragut Ave (Baldwins Run) sewage treatment plant, activated-sludge process, Camden, N. J.

EFFLUENT TREATMENTS

Effluent treatments, set up to screen the materials selected for testing, varied according to the material. Testing procedures included batch or jar tests, columnar beds, and sludge blanket treatments. The screening tests were designed so as to place the effluent samples in contact with a given material in a manner that could be duplicated (for testing and comparing effects of similar materials). Time factors were held constant to simulate practical detention times in an actual treatment. The ratio of the weight of the treatment material under study to the weight

of the effluent being treated was varied, especially if an initial test of the material indicated the pertinency of determining Freundlich isotherm data for an economic evaluation of indicated treatment dosages.

When screening data indicated that a material was potentially useful for lowering the refractory-contaminant content of the effluent, combination treatments (often involving the use of conventional water treatment chemicals) were tried. These multicomponent treatments were designed to establish:

(a) Whether or not this promising material is removing the same contaminants as the complementary treatment materials, and
(b) whether or not synergistic effects can be produced in a system wherein the promising material is employed.

Most of these multicomponent treatments involved simultaneous treatment of the effluent by the materials in a one-stage treatment. Some tests were, however, conducted in a series of stages wherein the effluent was treated first with one material, then with another, and so on.

Synthesis and testing of novel compounds and materials were undertaken during this study. These novel products were prepared from cheap, commercially available raw materials in an effort to:

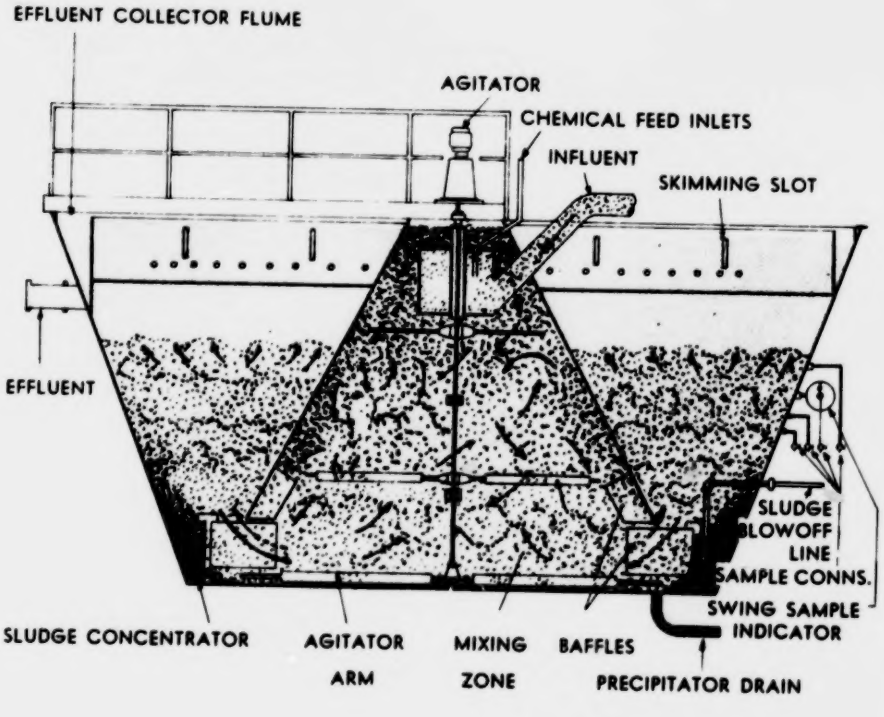
(a) Enhance previously established properties of refractory-contaminant removal possessed by the raw materials, and
(b) adapt a material (or materials) in a way that would overcome inherent disadvantages of its use in the sludge blanket process or other continuous-flow systems (Figure 3).

TECHNICAL DISCUSSION

Nature of Materials To Be Removed

Secondary waste-water effluents generally contain only about 0.05 percent of materials other than water.[2] Various efforts to analyze these materials have resulted only in pinpointing a few according to their exact composition. Many must, therefore, be listed according to similar structural groups or other characteristics. Some of these contaminants have been found to be ABS, proteins, carbohydrates, tannins, lignins, long-chain hydrocarbons, and long-chain fatty acids. Essentially they are anionic or nonionic organic materials. Some

inorganic materials, notably chlorid , are also represented here.



--copyright THE PERMUTIT COMPANY, 1955

Figure 3. PERMUTIT PRECIPITATOR showing thorough mixing of chemicals with influent and previously formed sludge.

Mechanisms of Removal Amenable to the Sludge Blanket Process

ADSORPTION AND ION EXCHANGE

Many of these contaminants can be adsorbed onto clays and other minerals. The adsorption process need not impart other contaminants to the effluent. Cationic resins (anion exchangers) will also reduce the concentration of these materials in secondary waste-water effluent. Three main problem areas are, however, encountered here: (1) Organic fouling, (2) disposal of regeneration wastes, and (3) removal of exchanged ions from the effluent. Anionic resins (cation exchangers) can be of some value in eliminating these materials from waste-water-plant discharge waters, especially in the H^+ form. The prime mechanism involved here is believed by the writers to be an "in situ" coagulation effect, wherein the coagulated materials are adsorbed or otherwise held onto the surface of the resin. If this is the case, this class of exchangers could hold much promise, since it would have fewer of the inherent disadvantages of the anion exchangers. It might be necessary, however, to present a cation exchanger to an effluent in a much more finely divided state than that of an anion exchanger.

COAGULATION

Coagulants and coagulant aids, ideally, would form the basis of a sludge blanket process for removal of refractory contaminants from waste-water effluents. Continuous coagulation, wherein a sludge blanket is built up and held constant, is the very heart of the sludge blanket process for water treatment. The coagulated solids present an enormous surface area for adsorption to take place. Finely divided solids, as well as liquids or solutions, can be simultaneously fed into the sludge blanket apparatus to supplement the work of the coagulants and coagulant aids in the removal of refractory contaminants. These supplementary additives can be oxidants as well as adsorbents or ion exchangers.

While continuous coagulation may be desirable, it is not essential. A material having the character of a sludge blanket can be prepared and utilized in the sludge blanket apparatus. The more complex the mixture contained in the sludge blanket apparatus the more difficult becomes the task of separating the components for regeneration and re-use, where applicable.

OXIDATION

Oxidation can be feasibly used in the sludge blanket process simultaneously with coagulation, adsorption, and ion exchange. Agents for increasing oxygen transfer can be employed to assist the oxidizing agents.

Materials and Formulations Tested via Batch, Columnar Bed, and Sludge Blanket Treatments

ADSORBENTS IN BATCH TESTING

Most of the adsorbents tested were samples obtained from commercial suppliers and manufacturers. The mean particle size was approximately 325 mesh, mostly ranging from 200 to 400 mesh. The following adsorbents were tested as received (without altering or modifying them in any way other than by grinding and screening when necessary):

(a) Aluminates
    Calcium aluminate
(b) Carbonates
    Limestone
(c) Carbons and coals
    Ionac C-150--sulfonated-coal-type cation exchanger
    Nuchar C-190-N--activated carbon, vegetable origin
    Animal charcoal (bone black)
(d) Ion exchange resins
    Ionac A-540 (Cl^- form)
    Ionac A-300 (SO_4^- form)
    Permutit ZP (K^+ form)

GPO 812-253-2

(e) Industrial wastes, by-products
- Flyash, boiler and chimney,
  - Ionac Chemical Co., Birmingham, N.J., Plant
- Flyash
  - Cincinnati Gas and Electric
- Cement (stack) dust
  - Southwestern Portland Cement Co.

(f) Metal oxides
- Ilmenite
- Rutile--milled and ceramic
- Bauxite--calcined and uncalcined
- Zirconium oxide

(g) Phosphates
- Calcium phosphate
- Monazite

(h) Silicas
- Diatomaceous earths
- Perlites
- Silica flour

(i) Silicates
- Kaolinite
- Aluminum--silicate pigments
- Panther Creek Bentonite
- Wyoming Bentonite
- Manganese zeolite
- Attapulgites
- Molecular sieve powder
- Vermiculite
- Mica
- Greensand
- Desertalc
- Decalso
- Yellow gel

(j) Sulfates--"Rare earth sodium sulfate" (a sulfuric acid extractive of monazite ore containing cerium).

The following adsorbents, as modified or prepared in the laboratory, were tested:

(a) Metal oxides
- Zirconia, hydrous ZrO_2

(b) Silicas
- Amine-treated, diatomaceous earth

(c) Silicates
- $ZnCl_2$-treated vermiculite
- H_3PO_4- treated, Panther Creek Bentonite
- $ZnCl_2$-treated, Wyoming Bentonite
- $Zr(SO_4)_2$-H_2SO_4-treated, Wyoming Bentonite
- Zr (SO_4)-H_2SO_4-treated, uncalcined, Pikes Peak clay
- $ZnCl_2$-treated greensand
- $ZnCl_2$-treated bauxite, uncalcined
- $ZnCl_2$-treated attacote

COAGULANTS AND COAGULANT AIDS IN BATCH TESTING

The following coagulants and coagulant aids were tested in accordance with the well-known techniques of water clarification by coagulation:

Reten
Separan 2610-A
Rosin amine D acetate
Isodecyl diethylene triamine acetate
Alum
Ferric sulfate
Ferric chloride
Proteins
Titanium tetrachloride
Calcium oxide

OXIDANTS AND OXYGEN TRANSFER AGENTS IN BATCH TESTS

The following oxidants were tested:

Air—with and without methyl isobutyl carbinol—as an oxygen transfer agent, added to the effluent
Ferrate—prepared in laboratory
Potassium permanganate
Sulfuric acid

COMBINATION BATCH TREATMENTS

The following agents were tried in combination:

Panther Creek Bentonite plus titanium tetrachloride
Ferric chloride followed by activated carbon (Nuchar C-115)
Potassium permanganate plus ferric chloride followed by activated carbon (Nuchar C-115)
Potassium permanganate followed by activated carbon (Nuchar C-115)
Rutile (milled) in sulfuric acid; plus barium carbonate, plus sodium carbonate, plus ferric chloride

COLUMNAR-BED TESTING

The following materials were tested in columnar beds:

Ion exchangers
- Ionac A-300--medium-base, granular anion exchanger
- Ionac A-540--strong-base, bead-type anion exchanger
- Ionac XLA-400--experimental, strong-base, bead-type anion exchanger
- Ionac A-260--weak-base, granular anion exchanger
- Ionac C-240 (H^+ form)--standard, sulfonated, polystyrene, bead-type cation exchanger

Modified proteinaceous materials
  Various combinations of proteins (casein, soybean protein, glutens, glues, or gelatins) with ferric compounds (ferric chloride or ferric sulfate), mineral acids, alum, and lime were tested; aldehyde crosslinking of these materials was emphasized for purposes of stability
Minerals
  Diatomaceous earth
  Synthetic zeolite, diatomite, and perlite treated with amine acetate
Activated carbon
  Ionac P-50

SLUDGE BLANKET TESTING

Only the more promising materials, as evidenced by results obtained in screening tests of the batch and columnar-bed types, were tested in the sludge blanket apparatus. The materials so tested were:

Modified proteinaceous materials hardened and unhardened
Titanium tetrachloride
Protein plus ferric sulfate (fed separately)
Protein plus ferric chloride (fed separately)
Protein plus titanium tetrachloride (fed separately)

METHODS AND RESULTS

General

As previously mentioned, the screening tests were designed to place the effluent samples in contact with a given material in a manner that could be duplicated with physically similar materials.

Although some work was done with synthetic laudromat effluent and Rancocas Creek water to evaluate specific parameters further, secondary effluent remained the principal liquor employed in these tests. Initially, the authors felt that the filtration of the secondary waste-water effluent through a fine paper, such as Whatman No. 5, would be undesirable for purposes of this study. The reasons for this belief were as follows:

(a) The particulate matter would be removed anyway in sludge blanket filtration.
(b) The particulate matter might enhance coagulation and adsorption effects in the sludge blanket treatment process.

(c) Filtration through Whatman No. 5 paper would produce effluents that would vary in their content of the more finely divided particles. The passage of these fine particles through the paper would be regimented by the thin film or "cake" of larger particles as it builds up on the surface of the filter paper. This cake would vary in porosity and thickness depending on (1) the amount of waste water passed through the paper, and (2) the quantitative distribution range of the particles in an effluent according to size and concentration, which will vary from one effluent sample to another.

We can cite the following results of COD tests on filtrate increments of secondary waste-water effluent as evidence that filtration of the effluent introduces a variable and that this variable makes it difficult to evaluate COD-lowering effects of treatments when the drop in COD is not too great.

Table 1. COD OF A FILTERED SECONDARY EFFLUENT[a] AS A FUNCTION OF THE VOLUME CONTINUOUSLY PASSED THROUGH WHATMAN NO. 5 PAPER

Volume, ml	COD, mg/liter
560	155
700	144
1,300	122

[a]Prior to filtration, the above effluent exhibited a COD of 246 mg/liter.

We began our testing procedures with unfiltered secondary effluent. This practice was virtually abandoned, however, for the use of prefiltered (Whatman No.5 paper) secondary effluent. This was done for the obvious purposes of preventing the reduction in COD due to filtration from being confused with reduction in COD due to treatment and of preventing fouling of the surfaces of the adsorbents by those particles to which these surfaces need not be exposed. It was done also for the more subtle purposes of contributing more data to those investigators whose work involves systems wherein prefiltering is necessary and of standardizing a phase of our testing procedure so that our data would be more easily compared with those of other investigators.

Insufficient data were accumulated, while we were using unfiltered liquor, to conclude whether or not the particulate matter can enhance removal of refractory contaminants via the

mechanism of adsorption, if appropriate additives are used. It is conceivable that these unfiltered solids would be beneficial in providing "seeding" effects to coagulation procedures, which would lessen the dosage requirements of some coagulants and coagulant aids. It is also conceivable that at least some oxidants, if applied to the effluent in the presence of these particles, would be required in larger dosages owing to oxidation of the particles.

Batch Testing of Adsorbents

SYNTHETIC LAUNDROMAT EFFLUENT

Initial testing was done to determine the expected action of various materials when employed in the sludge blanket filtration process for removal of refractory contaminants from waste waters, especially secondary effluents. The objects of these tests were as follows.

(a) Establish a desirable range of particle size, in the case of solid adsorbents, to prevent carryover during startup.
(b) Compare the effects on waste-water effluent of various materials that can be used in the sludge blanket filtration process.
(c) Establish detention time for continuous treatment of a given increment of effluent within the equipment.

Two Spaulding-type laboratory bench model precipitators were set up (Figure 4) as described and depicted in a paper by Carpenter and Porter.[4] The precipitators were tested to ascertain the most desirable adsorbent particle size for use therein. It was determined that particles of from 5 to 50 microns in diameter should be used in the testing of insoluble solid materials in these precipitators in the absence of a coagulant. Particles of this size appear to be large enough, so that they do not wash out of the apparatus in the effluent. They are also small enough to assure that their properties of adsorption and ion exchange will be satisfactorily utilized.

Initial tests were run to learn what improvement might be expected in naturally occurring materials if they were activated with mineral acids. The tests were simple, consisting of rocking the effluent-adsorbent mixture from side to side in a half-full 1-liter jar (tilting down and then up to a 45° angle 50 times) then allowing to settle for 20 minutes. In lieu of waste-water effluent, which had not been obtained at that stage, a synthetic "laundromat" effluent was used containing 60 ppm of alkylbenzenesulfonate and a proportionate amount of phosphates as is found in commercial detergents. Five-hundred-milliliter portions of this effluent

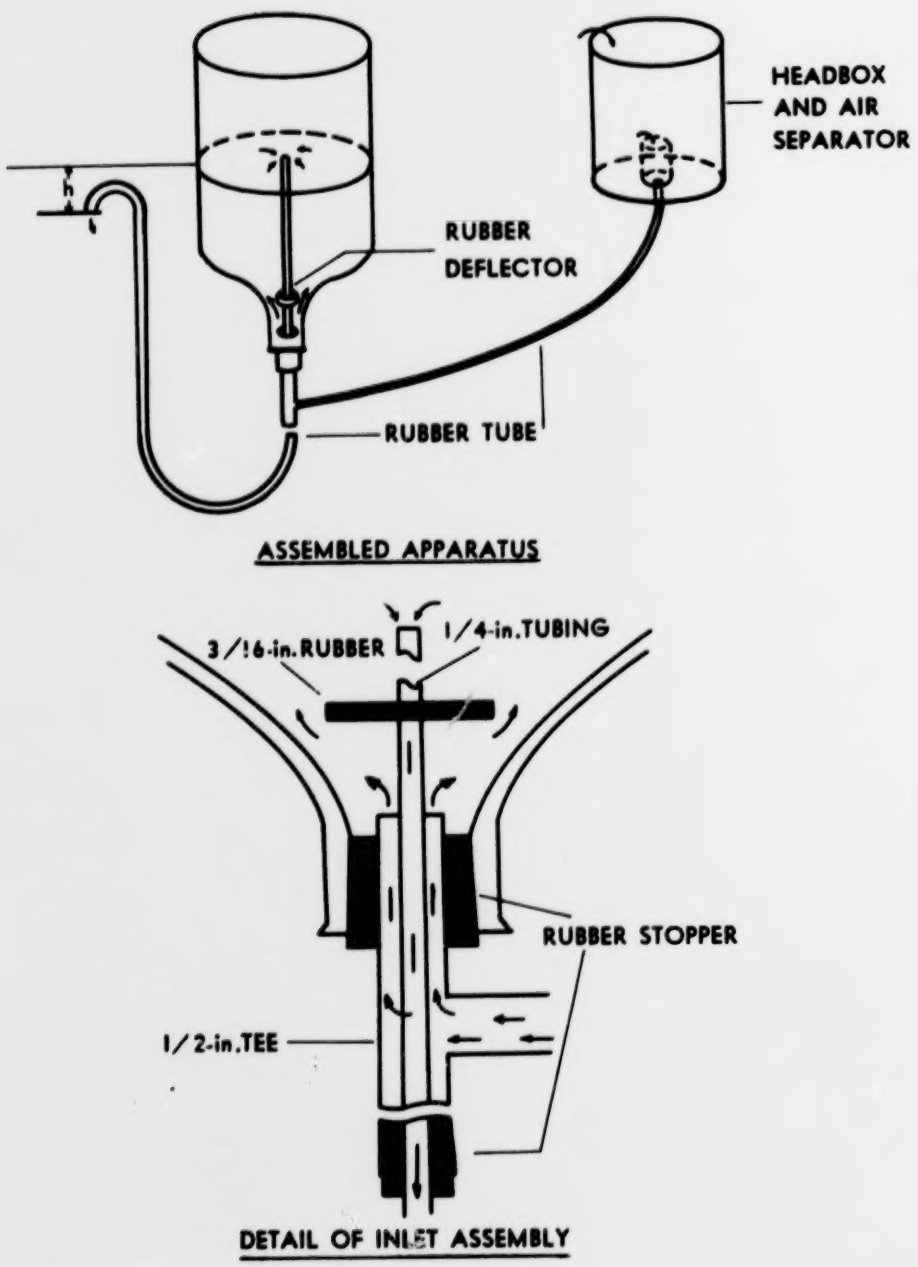


Figure 4. Schematic diagram of laboratory model of Spaulding-type precipitator.[4]

(containing 0.03 g ABS) were treated with 0.03 and 0.12 gram of adsorbent. The results are shown in Table 2.

Table 2. EFFECT OF SOME ADSORBENTS ON A SYNTHETIC LAUNDROMAT EFFLUENT CONTAINING 60 ppm ABS

Adsorbent, g	Residual ABS, ppm
Panther Creek Bentonite, 0.03	47
Panther Creek Bentonite, 0.12	47
Panther Creek Bentonite (H_3PO_4 activated) 0.03	32
Panther Creek Bentonite (H_3PO_4 activated) 0.12	32
Activated carbon, pulverized (coal product) 0.03	60
Activated carbon, pulverized (coal product) 0.12	25

UNFILTERED SECONDARY EFFLUENT

A 5-gallon sample of the finished effluent from the Mt. Holly, N. J., Sewage Plant was obtained and analyzed for chemical oxygen demand (COD), total solids, and nonvolatile solids after 2 hours at 500°C. This effluent had a COD of 206 milligrams per liter, a total solids content of 400 ppm, and a nonvolatile solids content of 270 ppm. After 1 week at room temperature the analyses had remained essentially unchanged.

Preliminary tests were run with several powdered adsorbents to compare their effect on the Mt. Holly waste-water effluent. The tests were run as with the synthetic mixture described above. Five-hundred milliliters of the effluent were treated with 0.208 gram of each adsorbent. This weight was selected, rather arbitrarily, because it represents the weight of the total solids content of 500 milliliters of the effluent. Settling times were varied.

It was determined that the 20-minute settling period following the rocking agitation was insufficient. Tests on the upper part of the settled effluents indicated that the "point of least returns" from settling occurred at about 30 minutes. For example, untreated effluent, with a COD of 206 milligrams per liter after settling for 20 minutes, had a COD of 186 milligrams per liter. After 30 minutes, the COD was reduced to 157 milligrams per liter, but after 90 minutes the COD was further lowered to only 151 milligrams per liter. After 90 minutes' settling, followed by filtration through a fast-flow grade of filter paper (E and D 615), the COD of the untreated effluent was further reduced to 141 milligrams per liter. By contrast, a treatment with 0.208 gram of Panther Creek Bentonite (American Colloid Co.), including a settling period of only 20 minutes and no filtration, lowered the COD to 122 milligrams per liter. The results of

similar tests with this and other naturally occurring adsorbents are shown in Table 3.

Table 3. ADSORBENT TESTING WITH UNFILTERED MT. HOLLY EFFLUENT

Adsorbent tested	Dosage, ppm	COD of untreated, unsettled, secondary effluent, mg/liter	Settling period, min.	COD after settling period, mg/liter	Total solids before treatment, %	Total solids after treatment, %	Nonvolatile solids before treatment, %	Nonvolatile solids after treatment, %
			0	206				
			20	186		0.036		
			30	157				
None	0	206	90	151	0.042			
Panther Creek Bentonite	416	206	20	122	0.042			
Wyoming Bentonite	416	206	20	139	0.042	0.045		
Hydrite "MP" kaolinite	416	206	20	127	0.042	0.036		
Natural, dried, uncalcined, diatomaceous earth	416	206	20	149	0.042	0.039		
Fullers Earth (attapulgite)	416	206	20	143	0.042	0.036		
Vermiculite	416	203	30	139				
Vermiculite	416	203	90	132				
None	0	184	90	131	0.038	0.035	0.025	0.025
Wyoming Bentonite	382	184	90	118	0.038	0.052	0.025	
Manganese zeolite	382	184	90	122	0.038	0.036	0.025	
Florex XXX (attapulgite)	382	184	90	112	0.038	0.033	0.025	
Desitalc	382	184	90	120	0.038	0.038	0.025	
Ionac C-150 carbon	382	184	90	129	0.038	0.034	0.025	
Flyash, chimney (Ionac, Bghm, N.J., plant)	382	184	90	125	0.038	0.034	0.025	0.022
Flyash, boiler (Ionac, Bghm, N.J., plant)	382	184	90	125	0.038	0.035	0.025	0.022
Ilmenite	382	184	90	127	0.038	0.033	0.025	

All these adsorbents were, to some extent, effective as tested in reducing the COD of the waste-water effluent beyond what could be expected by mere settling. No significant decrease in the total solids content of the waste-water effluent was noted in this preliminary testing of adsorbents.

SECONDARY EFFLUENT PREFILTERED THROUGH WHATMAN NO. 5 PAPER

The preliminary testing procedure with unfiltered secondary effluent left much to be desired as a standard procedure for purposes of comparative testing of adsorbents. While prefiltration of the effluent through a fine paper (Whatman No. 5) may

produce somewhat variable liquors, it can nevertheless be expected to remove particles that would settle in less than 90 minutes. Prefiltering of the effluent serves, therefore, to eliminate some doubt about whether the materials removed from waste water during the adsorbent tests were in solution or were present as finely divided solids.

Prefiltering of the effluent through Whatman No. 5 paper was begun and adhered to for the balance of this study, almost without exception. In addition, all batch adsorbent testing that followed the aforementioned preliminary tests were conducted as follows: 500 milliliters of filtered (Whatman No. 5 paper) secondary effluent were placed in a 600-milliliter beaker. A weighed amount of the adsorbent to be tested was placed in the waste water. The mixture was agitated at 50 rpm for 50 minutes with a paddle agitator device (see Figure 5). After this contact period, the treated effluent was filtered through E and D 615 paper. The filtrate was then tested for refractory contaminants as indicated by the test for COD (along with any supplementary tests deemed pertinent). This result was compared with the values on the untreated, filtered effluent.

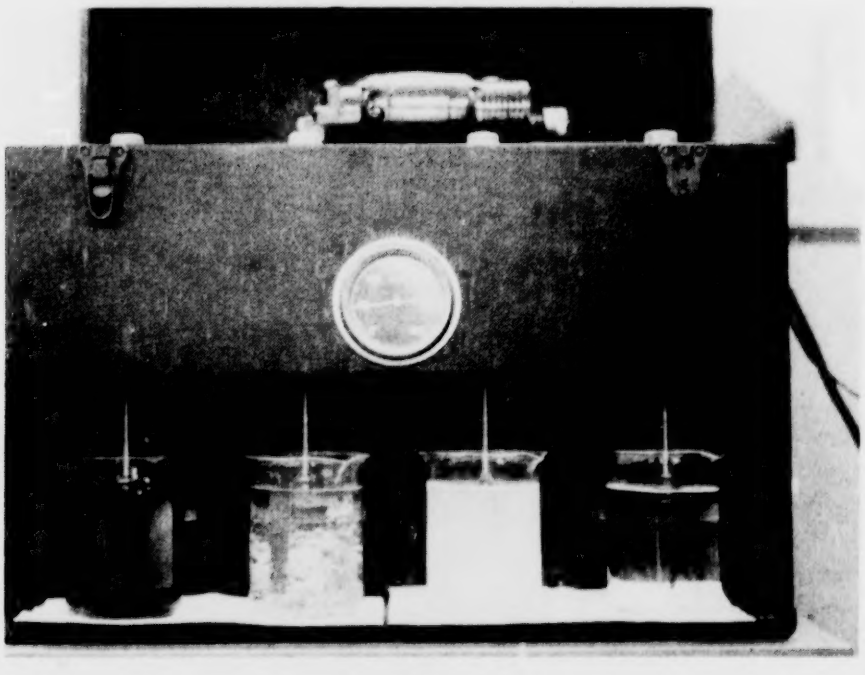


Figure 5. Jar-type batch testing apparatus. Beakers (left to right): (a) Activated carbon treatment, (b) protein-ferric compound coagulation, (c) lime treatment, (d) treated water.

Before these procedures were adopted, tests were run to establish the comparative effects of a postsettling period versus

a postfiltration through E and D 615 filter paper. Activated carbon (Nuchar C-190-N) powder was selected for these tests. The procedures employed and the results of these tests are presented in Table 4.

This method of comparing adsorbents was also employed to determine whether prechlorination of secondary effluent can be expected to have an effect on an adsorbent treatment. Nuchar C-190-N powder was again selected for use in comparative studies of chlorinated versus unchlorinated waste water.

Table 4. COMPARISON OF POSTFILTRATION VERSUS POST-SETTLING PERIOD ON TREATED EFFLUENT

Effluent used in test	Treatment	COD after treatment, mg/liter
Secondary effluent. Not prefiltered. Initial COD = 246 mg/liter	(1) Contacted for 50 minutes at 50 rpm with 400 ppm of Nuchar C-190-N activated carbon, postfiltered through E and D 615 paper; no settling period.	109
	(2) Contacted for 50 minutes at 50 rpm with 400 ppm of Nuchar C-190-N activated carbon, settled for 16 hours. No post-filtration.	115
Secondary effluent. Prefiltered through Whatman No. 5 paper. Initial COD (after prefiltration) = 140 mg/liter	(3) Same as Treatment (1) above	80
	(4) Same as Treatment (2) above	81

A 1/2-gallon sample of Mt. Holly effluent was taken immediately prior to chlorination and another immediately after chlorination. The time lag between these samples approximated the time interval during which the effluent passed from the point at which it was sampled prior to chlorination to the point at which it was sampled after chlorination. Tests on these samples were completed within 4 hours after sampling. These tests revealed

no significant differences between the chlorinated and unchlorinated effluents that would appreciably affect the COD test or the adsorption of contaminants by activated carbon. In Table 5 the tests run on these effluent samples and the results are outlined.

Table 5. A COMPARISON OF CHLORINATED AND UNCHLORINATED MT. HOLLY SECONDARY EFFLUENT

	Unchlorinated, mg/liter	Chlorinated, mg/liter
COD of unfiltered effluent	208	223
COD of effluent filtered through Whatman No. 5 paper	82.4	84.4
Cl^- correction to above COD values	10.0	12.9
Net COD of filtered effluents	72.4	71.5
Cl^- of filtered effluent	43.3 ppm	56.1 ppm
COD of filtered effluent (Whatman No. 5 paper) treated with 500 ppm Nuchar C-190-N	28.7	30.6
Cl^- correction to COD of carbon-treated effluents	11.1	12.2
Net COD of carbon-treated effuents	17.6	18.4
Cl^- of filtered, carbon-treated effluent	48.1 ppm	52.9 ppm

The adsorbents tested via these batch treatment procedures (without prior modification of the adsorbents) and the results of each test are outlined in Table 6.

Attempts were made to enhance the adsorptivity of some cheap materials by modifying them or imparting other materials onto them. The results obtained in batch testing of these materials are also tabulated in Table 6.

Some of the natural materials were treated with a 20 percent aqeous zinc chloride solution for 10 minutes, washed, and dried, then used to treat filtered waste-water effluent. Results

Table 6. ADSORBENT TESTING WITH SECONDARY EFFLUENT, PREFILTERED THROUGH WHATMAN NO. 5 PAPER, AGITATED AT 50 rpm FOR 50 MINUTES, AND THEN POSTFILTERED WITH E AND D NO. 615

A. Materials tested as received		Dosage, ppm	COD of effluent before test, mg/liter[a]	COD of effluent after test, mg/liter[a]	COD-lowering effect, mg/liter
Aluminates	Calcium aluminate	1,000	66	65	1
Carbonates	Limestone	20,000	42	42	0
Carbons and coals	Animal charcoal (bone black)	1,000	66	51	15
	Nuchar C-190-N	1,000	128	43	85
		650	81	20	61
		500	103	44	59
		500	103	42	61
		500	77	34	43
		500	69	10	59
		500[b]	63	0	63
		500[b]	75	7	68
		500[b]	56	0	56
		400	143	68	75
		375[b]	47	7	40
		300[b]	47	6	41
		250[b]	56	7	49
		200	128	103	25
Ion exchange resins	Ionac A-540 (Cl-form)	500[b]	51	3	48
	Ionac A-300 (SO_4-form)	300[b]	47	31	16
Industrial wastes, by-products	Flyash-Cincinnati Gas and Electric	20,000	44	40	4
	Cement (stack) dust-South Western Portland Cement Co.	20,000	44	36	8

Metal oxides	Rutile, milled	4,000	66	64	2
	Rutile, ceramic	4,000	66	62	4
	Bauxite, calcined	1,386	122	125.5	0
	Bauxite, uncalcined	1,386	122	125.5	0
	Zirconium oxide, dried	650	93	91	2
Phosphates	Monazite	1,386	125	121	4
Silicas	Diatomaceous earth	650	81	79	2
	Dicalite 426 (perlite)	5,000	85	81	4
	Dicalite 4106 (perlite)	5,000	85	81	4
	Dicalite 4156 (perlite)	5,000	85	83	2
	Celite 545 Mix A	5,000	78	70	8
	Celite 545 Mix B	5,000	78	68	10
	Celite 545 Mix C	5,000	78	70	8
	Celite 545 Mix D	5,000	78	68	10
	Florisil	20,000	44	40	4
Silicates	Florex XXX	1,386	125	100	25
	Attacote	2,000[b]	62	40	22
	Attacote	1,386	110	96	16
	Attacote	500[b]	74	57	17
	Attacote	250[b]	55	52	3
	Attasorb LVM	10,000	46	60	--
	Attasorb RVM	5,000[b]	53	62	--
	Attaclay	500	58	52	6
	Attagel 20	5,000[b]	53	62	--
	X-250 (mineral plus chemical, Phillip Co.)	5,000[b]	53	62	--

Table 6. (Continued)

A. Materials tested as received		Dosage, ppm	COD of effluent before test, mg/liter[a]	COD of effluent after test, mg/liter[a]	COD-lowering effect, mg/liter
	Greensand	2,000	95	90	5
	Greensand	500[b]	63	54	9
	Greensand	250	95	95	0
	Edgar ASP 900	10,000	44	51	--
	Edgar ASP 101	20,000	69	51	18
	Edgar ASP 403	500	58	58	0
	Edgar ASP 602	500	58	55	3
	Vermiculite	692	132	124	8
	Mica-waterground	10,000	42	42	0
	Panther Creek Bentonite	400	128	120	8
	Molecular sieve powder, type 13X	2,000[b]	53	51	2
	Yellow gel	4,000[b]	51	46	5
	Decalso	2,000[b]	51	53	--
Sulfates	"Rare earth sodium sulfate" (a sulfuric acid extractive of monazite ore, containing cerium)	2,000	115	117	--

B. Laboratory prepared or modified materials	Dosage, ppm	COD of effluent before test, mg/liter[a]	COD of effluent after test, mg/liter[a]	COD-lowering effect, mg/liter
Wyoming Bentonite, $ZnCl_2$- treated	1,000	98	91	7
Greensand, $ZnCl_2$- treated	500	98	94	4
Bauxite, uncalcined, $ZnCl_2$- treated	500	96	92	4
Vermiculite, $ZnCl_2$- treated	500	89	89	0
Attacote, $ZnCl_2$- treated	500	89	75	14
Wyoming Bentonite, $Zr(SO_4)_2$-H_2SO_4-treated	5,000	84	52	32
Uncalcined Pikes Peak clay, $Zr(SO_4)_2$-H_2SO_4- treated	5,000	84	63	21
Hydrous zirconia	3,075[c]	44	16	28
Hydrous zirconia	692[be]	63	50	13
Isodecyl diethylene triamine imparted onto diatomaceous earth	4,000	81	159	--

[a]Corrected for chlorides.
[b]Camden effluent.
[c]As ZrO_2.

were not promising, but this, together with known anion-exchanging properties of certain zirconium compounds, led to testing of some zirconium-treated materials. Hydrous zirconia, which is known to possess these properties, was freshly prepared in the laboratory by mixing $Zr(SO_4)_2$ and NaOH solutions, then washing the precipitate. The moist precipitate was used to treat filtered waste water by the batch-testing procedure.

Powdered Wyoming Bentonite and uncalcined Pikes Peak clay were agitated for 10 minutes in a 20 percent aqueous solution of $Zr(SO_4)_2 \cdot 4H_2O$ containing about 1 percent H_2SO_4 on the total solution weight. The clays were then filtered, washed thoroughly with distilled water, and dried. The dry, treated clays were then ground in a mortar and used to treat filtered waste-water effluent. A comparison of the COD values of the waste-water effluent before and after treatment indicates that zirconium-treated clays, notably Wyoming Bentonite, remove considerably more COD-imparting materials that they do when not treated. The zirconium-treated Wyoming Bentonite also appears to compare favorably with hydrous zirconia in lowering the COD of filtered waste water. The performance of Nuchar C-190-N was not, however, matched by zirconia or zirconium-treated clays.

A sparsely soluble, alkylated polyamine was imparted onto diatomaceous earth and tested to establish whether or not it would remove waste-water contaminants. It was hoped that this amine would adhere to the diatomaceous earth, without the necessity of crosslinking, and pick up COD-imparting contaminants, but this apparently was not the case. Rather than lower the COD, a batch treatment of waste water with this material considerably increased the COD. The amine employed here was isodecyl diethylene triamine. The thought was that the amine and adsorbed materials could be burned off and the base carrier re-used.

Attempts were made to convert a wood shaving and sawdust mixture into a cheap adsorbent by treatment with: (a) Sodium bisulfite, or (b) sodium hypochlorite followed by ammonia. The $NaHSO_3$ treatment was done to try to effect a mild sulfonation of the wood, while the $NaOCl$-NH_3 treatment was tried in the hope of incorporating weakly cationic groups into the wood structure.

In general, the procedure followed was to make up an aqueous solution of the compound, place the wood into it, add sufficient water to just cover the wood, mix thoroughly, and allow several hours' contact time. After the contact period, the treated wood was washed with demineralized water. In testing the adsorptivity of the washed, treated wood, a weighed, damp portion was added to the waste water and, after treatment, was removed, washed, dried, and reweighed to establish the dosage used, on the dry basis.

GPO 812-253-?

Sodium Bisulfite-Treated Wood

A mixture of wood shavings and sawdust was soaked at room temperature in a 4.5 percent solution of sodium bisulfite as $NaHSO_3$. After 40 hours, a portion of the mixture was washed with demineralized water. Then 10,800 ppm (dry basis) of the washed, treated wood was used to treat filtered waste-water effluent with a COD of 85 milligrams per liter. This treatment raised the COD to 191 milligrams per liter. After an additional 120 hours in contact with the $NaHSO_3$, another portion of the treated wood was washed. The test was repeated, this time by using 2,600 ppm (dry basis) of the wood on effluent with a COD of 72 milligrams per liter. This treatment raised the COD by 42 milligrams per liter to a value of 114 milligrams per liter. A "blank" was also run, by using 2,300 ppm of the treated wood (dry basis) on demineralized water with no COD. The purpose of the blank was to measure the extent to which the wood yielded oxidizable materials to the solution. The treated wood imparted 33 milligrams per liter of the COD to the demineralized water. Theoretically, the COD of demineralized water, treated as in the case of the waste water with 2,600 ppm of the wood (instead of 2,300 ppm), would be 35 milligrams per liter. On the assumption that 35 milligrams per liter COD would also have been imparted into the waste water, and not 42 milligrams per liter, the possibility of an exchange of wood components for waste-water components becomes apparent. In attempts to verify this, however, no chloride or sulfate could be exchanged for wood components.

Sodium Hypochlorite- and Ammonia-Treated Wood

The $NaOCl$-NH_3 treatment of the wood mixture was done as follows: Ten grams of NaOCl in aqueous solution was mixed with demineralized water in an amount estimated to be sufficient to wet 90.0 grams of the wood. Ninety grams of the wood was then placed into this mixture, and sufficient additional water was added to just cover the mixture. After thorough mixing, a 20-hour contact time was allowed, then the mixture was washed with demineralized water. After washing, 15.0 grams of NH_3 in a 29 percent aqueous solution was added to the wood. After 4 hours' contact time, the mixture was divided into two portions. One portion was left in contact with the NH_3 for 72 more hours, while the other portion was immediately washed free of excess NH_3. Then 4,000 ppm (dry basis) of the wood having 4 hours' contact with the NH_3 was used to treat 500 milliliters of filtered waste-water effluent with a COD of 72 milligrams per liter, and 500 milliliters of demineralized water with no COD value. After this treatment, the COD of the waste-water effluent was 81, and that of the demineralized water was 12 milligrams per liter. This indicated a possible COD reduction of 3 milligrams per liter,

on the assumption that the COD imparted by the treatment was not owing to refractory materials and could have been easily removed by aeration, etc. It was also ascertained that no chloride or sulfate could have been exchanged for any SO_2 or NH_3 that might have been incorporated into the components of the wood. Longer contact times with the ammonia gave no better results. This procedure was also tried with 5.0 grams of NaOCl to 95 grams of wood with no more success.

Batch Testing of Coagulants and Coagulant Aids

GENERAL PROCEDURE

The testing procedure for coagulants was much the same as the procedure employed with the solid adsorbents. A 500-milliliter portion of the filtered waste water was placed in a 600-milliliter beaker and agitated at 100 rpm. The coagulant was then added and the speed of agitation was reduced to 50 rpm. The overall contact time with agitation was 50 minutes, during which time pH adjustments with acids or bases or both, were made when deemed necessary.

After the contact period, the treated effluent portions were filtered through E and D 615 paper.

The batch-testing procedures, employed with adsorbents and coagulants, as well as with oxidants (which are considered later) were intended to be as similar as possible for the purpose of comparing results. The results of the batch coagulant tests are summarized in Tables 7 and 8.

ORGANIC MATERIALS

Many organic coagulants and coagulant aids are commercially available. Synthetic products, especially the polyelectrolytes, are employed in water treatment in very modest dosages. They can, therefore, be regarded as being relatively cheap by virtue of the fact that, when applicable, they do not contribute substantially to the overall treatment cost. This is true, even though the price per pound of these materials is much higher than the price per pound of most inorganic coagulants, such as lime, ferric chloride, and alum. For example, dosage requirements of only 5 to 10 ppm are common for these organic materials, while dosages of 30 to 100 ppm are required for many inorganic coagulants. Moreover, costly pH adjustments are often avoidable when these materials are used.

Evaluation of the effect of these materials in treatment of secondary waste-water effluent is difficult because of their solubility. Any excess of an organic coagulant or coagulant aid that remains in solution following a treatment contributes to the

Table 7. COAGULANTS AND COAGULANT AIDS IN BATCH TESTING

	Dosage, ppm	COD of effluent before test, mg/liter[a]	COD of effluent after test, mg/liter[a]	COD-lowering effect, mg/liter	Remarks
Reten	10	76	67	11	
Separan 2610-A	4	194[b]	208[b]		
$FeCl_3$	15	66	43	23	
$FeCl_3$	30	66	39	27	
$FeCl_3$	60	97	65	32	pH of $FeCl_3$ tests adjusted to 3.0
$FeCl_3$	90	66	37	29	
$FeCl_3$	60	97	65	32	
$FeCl_3$	150	102	50	52	
Ferric sulfate	30	129	88	41	
Ferric sulfate	60	134	89	45	pH of $Fe_2(SO_4)_3$ tests adjusted to 3.0
Ferric sulfate	90	137	66	71	
Alum	30	66	57	9	pH of alum tests adjusted to 6.0
Alum	60	102	100	2	
Alum	60	66	56	10	
Alum	90	66	55	11	
Titanium tetrachloride	140	102	73	29	pH 5.75 after addition of $TiCl_4$, no adjustment made

[a]Corrected for chlorides.

[b]Secondary effluent was as received with no fine-paper filtration. Values shown are results after a 90-minute settling period followed by filtration through E and D 615 paper.

Table 8. BATCH COAGULATION TESTING OF PROTEINS AND PROTEIN PRODUCTS.

PART A. GLUTEN FEED SUPPLEMENT AND CASEIN

Treatment No.	COD of untreated, filtered effluent, corrected for chlorides, mg/liter	Treated with	Dosage,[a] ppm	COD after treatment, corrected for chlorides, mg/liter	Drop in COD due to treatment, mg/liter	Remarks
1	0 (Tap water)			0		COD run on tap water as a blank
2	0 (Tap water)	Mix No. 1 $FeCl_3$	100 60	15		Protein mixture added to effluent, stirred briefly, then ferric compound added; no pH adjustment made
3	101	Mix No. 1 $FeCl_3$	100 60	115		Same procedure as in Treatment No. 2
4	101	Mix No. 1 $FeCl_3$	100 60	81	20	Same procedure as Treatment No. 2, but pH adjusted to 3.2 with 5% H_2SO_4 following addition of the ferric compound
5	97	$FeCl_3$	60	64.5	32.5	Ferric compound added, stirred briefly, then pH adjusted to 3.3
6	97	Mix No. 2 $FeCl_3$	100 60	99		Same procedure as Treatment No. 4

7	0 (Tap water)	Mix No. 2	100	16	—	Same procedure as Treatment No. 4
		$FeCl_3$	60			
8	96	Mix No. 3	500	71	25	Same procedure as Treatment No. 2
		$FeCl_3$	225			
9	96	Mix No. 3	100	55	41	Same procedure as Treatment No. 2
		$FeCl_3$	60			
10	102	Mix No. 3	100	77	25	Protein added, stirred briefly, pH adjusted to 3.2 with 1:1 HCl
11	102	Mix No. 3	50	80	22	Same procedure as Treatment No. 10, but postfiltered (Whatman No. 42) owing to fineness of floc
12	102	Mix No. 3	50	46	56	Protein added, stirred briefly, pH adjusted to pH 3.2 with 1:1 HCl, agitated at 50 rpm for 30 minutes, ferric compound added, and agitation continued for 20 minutes more
		$FeCl_3$	30			
13	102	Mix No. 3	25	82	20	Same procedure as Treatment No. 4
		$FeCl_3$	15			

Table 8. Part A (continued)

Treatment No.	COD of untreated, filtered effluent, corrected for chlorides, mg/liter	Treated with	Dosage,[a] ppm	COD after treatment, corrected for chlorides, mg/liter	Drop in COD due to treatment, mg/liter	Remarks
14	129	Mix No. 3 $Fe_2(SO_4)_3$	50 30	91	38	Same procedure as Treatment No. 12
15	129	$Fe_2(SO_4)_3$	30	88	41	pH adjusted to 3.1 with 5% H_2SO_4, stirred briefly, then $Fe_2(SO_4)_3$ added
16	134	Mix No. 3 $Fe_2(SO_4)_3$	50 30	89.5	44.5	Same procedure as Treatment No. 12, but pH adjustment made with 5% H_2SO_4
17	134	Mix No. 3 $Fe_2(SO_4)_3$	50 30	99	35	Same procedure as Treatment No. 4
18	134	Mix No. 3 $Fe_2(SO_4)_3$	50 60	84	50	Same procedure as Treatment No. 4
19	134	$Fe_2(SO_4)_3$	60	89	45	Same procedure as Treatment No. 5

20	137	Mix No. 3 $FeCl_3$	50 30	87	50	Same procedure as Treatment No. 12, but pH adjustment made with 5% H_2SO_4
21	137	Mix No. 3 $Fe_2(SO_4)_3$	50 30	105	32	Protein added, agitated for 20 minutes at 50 rpm, then ferric compound added and agitation continued for 20 minutes more, then pH adjusted to 3.1 with 5% H_2SO_4 and agitation continued for 10 minutes more
22	137	Mix No. 3 $Fe_2(SO_4)_3$	50 60	90	47	Same procedure as Treatment No. 21
23	137	$Fe_2(SO_4)_3$	90	66	71	Same procedure as Treatment No. 15
24	137	Mix No. 3 $FeCl_3$	50 30	74	63	Conditions similar to Treatment No. 12, but time intervals not strictly adhered to, and pH adjustment made with 1:1 HCl

Table 8. (continued)

PART B. ZEIN, CASEIN, AND SOYA TREATMENTS

Treatment No.	COD of untreated, filtered effluent, corrected for chlorides, mg/liter	Treated with	Dosage,[a] ppm	COD after treatment, corrected for chlorides, mg/liter	Drop in COD due to treatment, mg/liter	Remarks
1	61	Mix No. 4 $FeCl_3$	50 60	39	22	Protein dispersion added to effluent, stirred briefly, then pH adjusted to 3.1 with 1:1 HCl; agitated 30 minutes; $FeCl_3$ added; agitated 20 minutes more
2	59	Mix No. 4 $FeCl_3$	50 60	35	24	Same procedure as in Treatment No. 1
3	61	Mix No. 4 $FeCl_3$	100 60	49	12	Same procedure as in Treatment No. 1
4	59	Mix No. 4 $FeCl_3$	100 80	43	16	Same procedure as in Treatment No. 1
5	59	Mix No. 5 $FeCl_3$	50 60	55	4	Same procedure as in Treatment No. 1
6	59	Mix No. 5 $FeCl_3$	100 80	103	(+44)	Same procedure as in Treatment No. 1
7	0 (Tap water)	Mix No. 4 $FeCl_3$	50 60	4	(+4)	Same procedure as in Treatment No. 1, but final pH adjustment made (to 6.2) with Na_2CO_3
8	0 (Tap water)	Mix No. 4 $FeCl_3$	100 80	11	(+11)	Same procedure as in Treatment No. 7

9	0 (Tap water)	Mix No. 5 $FeCl_3$	50 60	14	(+14)	Same procedure as in Treatment No. 7
10	0 (Tap water)	Mix No. 5 $FeCl_3$	100 80	3	(+3)	Same procedure as in Treatment No. 7
11	64	Mix No. 4 $FeCl_3$	50 60	45	19	Protein added to effluent, mixture agitated 5 minutes, then pH adjusted to 3.1 with 1:1 HCl; mixture agitated 15 minutes more, then $FeCl_3$ added; mixture agitated an additional 15 minutes, then pH adjusted to 6.2 with $Ca(OH)_2$
12	64	Mix No. 4 $FeCl_3$	100 80	34	30	Same procedure as in Treatment No. 11
13	64	Mix No. 5 $FeCl_3$	50	44	20	Same procedure as in Treatment No. 11
14	64	Mix No. 5 $FeCl_3$	100 80	39	25	Same procedure as in Treatment No. 11
15	101	Mix No. 6 $FeCl_3$	50 30	61	40	Protein added to waste water, pH adjusted to 3.3 with HCl; agitated 30 minutes; $FeCl_3$ added and agitated 20 minutes more

Table 8. (continued)

PART C. FOOD-GRADE GLUTEN TREATMENTS

Treatment No.	COD of untreated, filtered effluent, corrected for chlorides, mg/liter	Treated with	Dosage,[c] ppm	COD after treatment, corrected for chlorides, mg/liter	Drop in COD due to treatment, mg/liter	Remarks
1	99	Mix No. 7 $FeCl_3$	75 45	56	43	pH adjusted with HCl to 2.9-3.1 range after adding gluten and $FeCl_3$; pH adjusted to 6.0-6.2 with CaO after coagulation and contact time
2	99	Mix No. 7 $FeCl_3$	100 60	61	38	Same as Treatment No. 1
3	99	Mix No. 7 $FeCl_3$	150 90	57	42	Same as Treatment No. 1
4	99	Mix No. 7 $FeCl_3$	200 120	56	43	Same as Treatment No. 1
5	98	Mix No. 7 $FeCl_3$	75 45	64	34	No neutralization after coagulation
6	98	Mix No. 7 $FeCl_3$	200 120	51	47	Same as Treatment No. 5
7	98	Mix No. 7 $FeCl_3$	75 45	52	46	Same as Treatment No. 1, but postadjustment to pH 6.5
8	98	Mix No. 7 $FeCl_3$	200 120	51	47	Same as Treatment No. 7

[a]Dosage values for Mixtures No. 1 and No. 2 were in ppm of the total mixture. Dosage values for Mixture No. 3 were in ppm of casein. Dosage values for $Fe_2(SO_4)_3$ were in ppm of $Fe_2(SO_4)_3$ calculated as ppm of $FeCl_3$. Consult text for material composition.

[b]Protein dosages based on weight of protein in dispersion.

[c]Gluten dosages based on weight of gluten in dispersion.

final COD of the treated effluent. Accurate testing procedures for each residual, synthetic, organic coagulant and coagulant aid in treated waste water are not currently available. Some measure of their effectiveness can, however, be gained, by limiting the testing of these materials to dosages in the 5 to 10 ppm range, and ignoring the contribution to the overall COD of their residue in solution.

This procedure cannot be followed in the case of proteins. Even the more hydrophobic proteins are difficult or impossible to precipitate in concentration of less than 25 ppm.

A test for residual protein, based on reduction of the protein and consequent production of gaseous N_2, is feasible. No emphasis was, however, placed on this test during this study because time was limited and because both the economic removal of the residual protein and the economic premodification of the protein (to prevent soluble fractions from being imparted into the treated effluent) were reasoned to be more immediately pertinent to the purposes of this study.

Proteins and protein products were extensively tested by tne batch coagulation procedure. During testing, variations in pH and in contact time before and after pH adjustment were tried with the purpose of learning how residual protein or residual organic materials from protein products can be minimized in the treated effluents. Coprecipitation of the protein with a ferric compound was stressed.

The following protein mixtures were used in these experiments:

Mixture No. 1; approximate composition:
- 5 parts NaOH
- 42 parts corn gluten
- 10 parts water
- 48 parts starches, oils, etc.

Mixture No. 2; approximate composition:
- 6 parts CaO
- 42 parts corn gluten (The gluten source was GLF 40% gluten feed supplement)
- 10 parts water
- 48 parts starches, oils, etc.

Mixture No. 3; composition:
- 20.0 grams of casein dissolved in 2 percent NaOH solution and diluted to 100 milliliters with 2 percent NaOH solution

Mixture No. 4 (dispersed zein):
10.0 grams zein (corn gluten protein) and
0.3 gram of NaOH in 100 milliliters of aqueous solution (heated to 70°C to effect dispersion)

Mixture No. 5 (dispersed casein):
10.0 grams of casein, 1.0 gram NaOH, diluted to 100 milliliters with water.

Mixture No. 6 (dispersed soya protein):
10.0 grams of soya protein diluted to 100 milliliters with 1 percent NaOH solution

Mixture No. 7 (dispersed gluten):
5 grams of 70 percent food grade gluten (100% basis) in a 200-milliliter aqueous NaOH solution; the gluten was preleached with 22 milliliters of 0.12N NaOH solution

Casein could not be precipitated from demineralized water at the 50 ppm level in the presence of 30 ppm $Fe_2(SO_4)_3$ when the pH was adjusted to 3.1 with H_2SO_4. Soya protein could not be precipitated from demineralized water at the 50 ppm level in the presence of 30 ppm $FeCl_3$ when the pH was adjusted to 3.3 with 1 : 1 HCl.

Coagulant testing controls were run by employing tap water, with no COD, in the belief that the electrolyte content therein might aid coagulation. The results of these protein coagulation studies are summarized in Table 8.

Rosin Amine D acetate was tested for its affinity for ABS in a synthetic laudromat effluent containing 60 ppm ABS. It was found that 33 ppm of Rosin Amine D acetate lowered the ABS content of this effluent to 10.9 ppm, and 66 ppm Rosin Amine D acetate lowered it to 1.7 ppm. The precipitate is essentially colloidal and could not be removed by an alum coagulation. A diatomite filtration with 1 percent diatomite on the weight of the effluent did, however, reasonably clarify the treated effluent.

Batch coagulation tests of the affinity of Rosin Amine D acetate for refractories in prefiltered (Whatman No. 5) wastewater effluent were tried. Dosage levels were at 25, 50, and 100 ppm of Rosin Amine D acetate. After each treatment the effluent was filtered by employing 1 percent diatomite on the weight of the effluent. A control was also run on the prefiltered waste water by measuring its COD after a similar diatomite filtration. The results of these tests are given in Table 9.

Similarly treated effluents were passed through beds of ion exchangers in an effort to remove any residual amine. These treatments are considered later.

Table 9. BATCH TREATMENT OF PREFILTERED SECONDARY EFFLUENT WITH ROSIN AMINE D ACETATE

Dosage of rosin amine D acetate, ppm	COD of effluent after treatment, mg/liter
None (control)	93
25	130
50	135
100[a]	

[a]Analysis not completed. Dichromate reduced more (much darker) in treated effluent than in control.

Batch treatments of (penta) isodecyl diethylene triamine acetate on both the 60 ppm ABS synthetic laudromat effluent and prefiltered waste water were tried. No precipitate resulted in either case, and no removal of ABS or other refractory contaminants was effected.

INORGANIC MATERIALS

The COD-lowering effects of lime (CaO), in varying dosages, on prefiltered (Whatman No. 5 paper) secondary effluents are summarized in Figure 6. Note that this curve bears more similarity to curves for solid adsorbents, for example, Nuchar C-190-N (Figure 7), than to other curves for other coagulants. The maximum effective dosages for both lime and Nuchar C-190-N, as indicated by these tests, appear to be about 500 ppm. By contrast, however, ferric chlorides, ferric sulfates, and alum are most effective at dosages of about 100 ppm. These coagulation tests with lime were carried out with no pH adjustments. That is, no effort was made to control the pH change effected by the lime itself.

Coagulation with ferric chloride and ferric sulfate is most effectively carried out at a pH level of about 3.0, and with alum at about 6.0. Accordingly, during this study, most coagulation that employed these coagulants involved pH adjustments with hydrochloric or sulfuric acids to obtain the desired pH. The results of the testing of $FeCl_3$, $Fe_2(SO_4)_3$, and $Al_2(SO_4)_3$ are given in Table 7.

Unlike ferric compounds and alum, titanium tetrachloride readily forms a floc in water with no adjustment in pH.

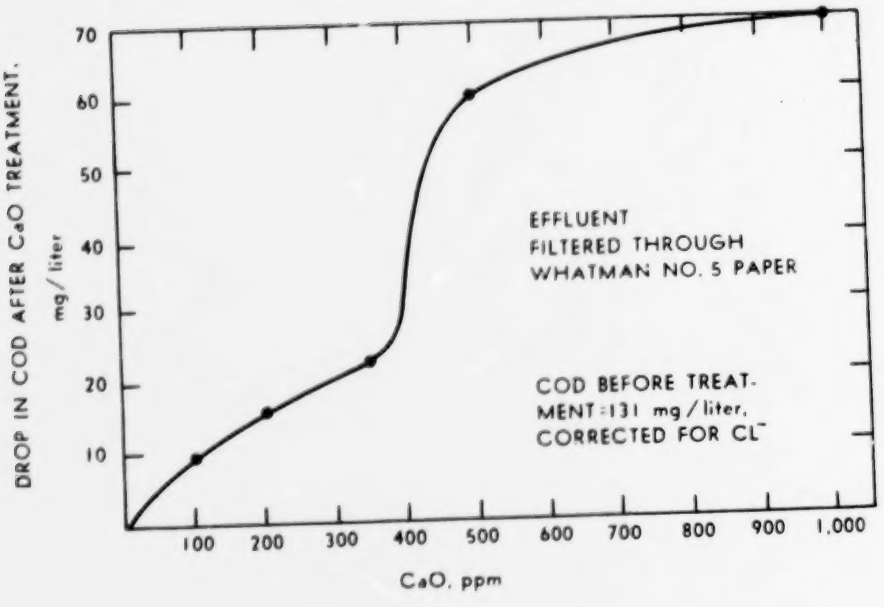


Figure 6. Lime treatment of filtered Mt. Holly secondary effluent.

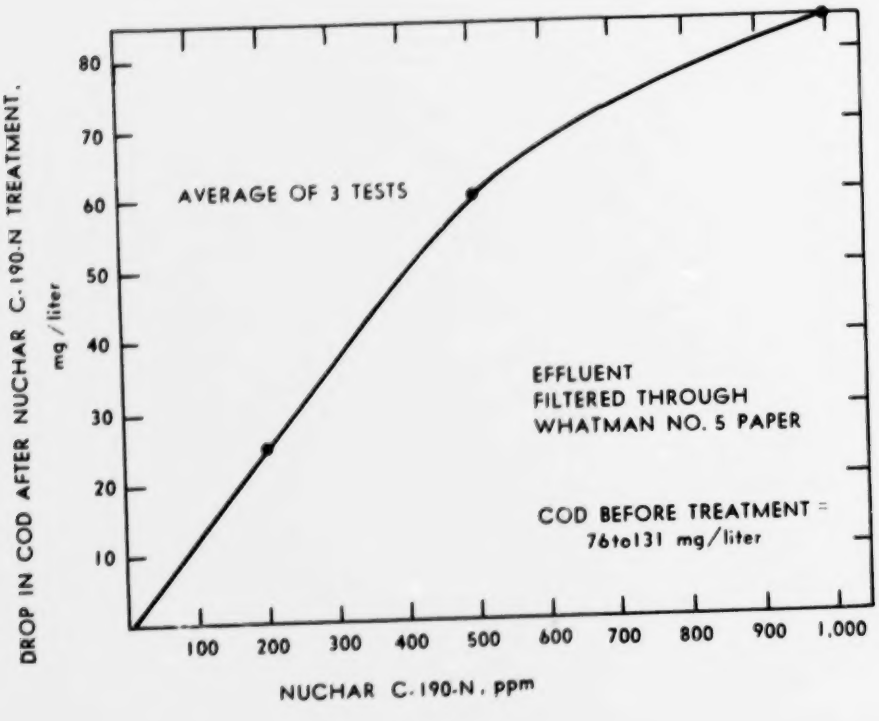


Figure 7. Nuchar C-190-N activated carbon treatment of filtered Mt. Holly secondary effluents.

Batch Testing of Oxidants and Oxygen Transfer Agents

Evaluation of the effects of oxidants and oxygen transfer agents on secondary effluent, as with organic coagulants and coagulant aids, is difficult. It was previously mentioned that the addition of an organic treatment agent to a secondary effluent can result in a residue of that compound being left in the effluent after treatment. In the case of organic materials, a falsely high COD can result. The same is true of some organic oxidants, while the reverse is true of some inorganic oxidants.

Ferrate VI, having hexavalent iron, was prepared from elemental Fe and $NaNO_3$.[3, 5] In the treatment of unfiltered secondary effluent, 592 ppm was employed by the technique used in the preliminary batch tests. That is, the sample was "rocked" 50 times, then left to settle for 90 minutes, after which it was filtered through E and D 615 paper. After this treatment, the COD of the effluent was 133 milligrams per liter. A control portion of the same effluent when settled for 90 minutes had a COD of only 116 milligrams per liter.

Potassium permanganate was tried as an oxidant by adding 30, 60, 90, and 120 ppm $KMnO_4$ to each of four 500-milliliter portions of unfiltered waste-water effluent. The portions were agitated with the paddle agitators for 50 minutes. The minimum dosed portion contained 30 ppm. The permanganate was not readily reduced. After 40 minutes, the characteristic pink tint was destroyed by the addition of a very minute crystal of cupric sulfate and of manganous chloride. The COD of the effluent after this treatment was 194 milligrams per liter. A control portion of the same effluent, when settled for 90 minutes, exhibited a COD of 117 milligrams per liter.

Hydrogen peroxide was tried as an oxidant on Mt. Holly secondary waste water that had been prefiltered through Whatman No. 5 paper. After the filtration, the COD of the effluent was 115 milligrams per liter. Ten ppm of H_2O_2 were added to a 500-milliliter portion of the filtered effluent and the mixture was agitated for 10 minutes at 50 rpm with a paddle agitator. After this treatment the COD had risen to 121 milligrams per liter. The main purpose of testing the effect of a peroxide on waste-water effluent was to learn if any reactions would occur that would render the refractory contaminants more easily removable by ion exchange. Batch tests employing a combination of a peroxide treatment with powdered ion exchange resin (Ionac A-540) were run and are considered later in this report.

The use of dispersed air in the presence of an oxygen transfer agent was also tested. This test was conducted with two 900-milliliter samples of unfiltered waste water, into which air

was passed by means of sintered-glass air dispersion tubes for a 2-hour period. Agitation was maintained at 160 rpm for this period. One of the samples was employed as a control, while 6.6 ppm of methyl isobutyl carbinol was added to the other prior to the period of bubbling and agitation. After the 2-hour treatment, both the control and the waste water containing methyl isobutyl carbinol were filtered through Whatman No. 5 paper. The COD of each was then measured. The control portion exhibited a COD of 80 milligrams per liter while the portion containing the carbinol had a COD of 82 milligrams per liter. The results of this test cannot be considered conclusive, however, since much foam was produced in both portions. This foam was removed because of its stability. It is possible that the methyl isobutyl carbinol dose was removed early during the bubbling-agitation period along with the foam.

In these tests of oxidants and oxygen transfer agents, higher COD values were recorded after treatment than before. Some explanation of this becomes apparent when the materials tested and the testing procedure are considered more closely. Residual H_2O_2 will reduce the hexavalent chromium in the COD test. In the case of Ferrate VI and $KMnO_4$ treatments, the rise no doubt results from the partial oxidation of particulate matter, which would have been removed by a Whatman No. 5 paper prefiltration. This partial oxidation of particulate matter could impart more soluble, incompletely oxidized, organic matter into the effluent than the overall oxidation treatment fully oxidized. While the testing procedures employed in evaluating oxidants leave much to be desired, it is believed that these approaches offer a more valid basis for comparing one oxidant with another at comparable dosage levels than does a procedure employing a prefiltration of the effluent. This belief is based on the need for specific tests to analyze and correct for the presence of residual treatment agents in treated effluents.

Batch Testing of Combinations of Materials

None of the batch treatments in this study were successful in removing all the materials that impart COD to secondary effluent. A few treatments, involving combinations of materials, were tried early in this study with secondary effluent that had not been prefiltered. The purpose of these tests was simply to learn if a batch treatment using additives could be expected to result in the treated effluent's having little or no COD. A batch test with a given dosage of an adsorbent will give an investigator only one point on a Freundlich Isotherm curve. Most of the materials on which batch tests were run during this study were tried at only one dosage level. Since one batch test had already

GPO 812-253-4

been run on these materials, further testing was done only when the material showed sufficient promise as a potential agent for economical removal of refractory contaminants from secondary effluent. Nevertheless, the Freundlich Isotherm curve, or even one point on it, is a useful criterion for the screening of adsorbents. The widespread use of the technique of Freundlich is, however, in itself an indication that investigators can rarely expect to effect complete removal of solutes from solution by batch treatments. These treatments are useful, rather, for comparison in examining more than one agent.

As previously indicated, in conducting a few of these combination tests, the writers were concerned more with formulating an opinion about the prospects of massive removal of organic contaminants from secondary effluent by batch procedures than with comparing the results of the treatments. The tests were conducted on unfiltered Mt. Holly secondary effluent, and the treated effluents were filtered through E and D 615 paper. Milled rutile was included in these treatments as a source of tetravalent titanium. $TiCl_4$ had exhibited an affinity for some of the organic refractories in waste water when precipitated, as TiO_2, in the effluent. The treatments and the results of each treatment are recorded in Table 10.

Hydrogen peroxide and powdered Ionac A-540 ion exchange resin (chloride form) were employed in other combination batch tests. In these tests, the secondary waste water was prefiltered through Whatman No. 5 paper. One portion was treated with H_2O_2 only, while another portion was treated with the A-540 only. Other portions were treated with H_2O_2 followed by A-540. The tests were of the usual jar type (with 50 minutes' agitation, in contact with the resin, at 50 rpm). Higher residual COD values were noted on waste water when the dual treatment was employed than when waste water was treated with the Ionac A-540 resin powder alone. The results of these tests are summarized in Table 11.

Columnar-Bed Testing

The use of columnar beds was included in these studies primarily for the testing of some insoluble polymeric materials. A batch treatment of secondary waste water, as previously discussed, cannot be expected to remove all refractory contaminants. These batch treatments provide the investigator, therefore, with no specific knowledge of the versatility of a material, that is, of the affinity of a given material for all or most of the refractory contaminants as opposed to an affinity for only one or two. Granted, there are some who may feel that an adsorbent or other agent that is specific for only one or two solutes when

Table 10. BATCH TREATMENTS EMPLOYING MIXTURES OF ADSORBENTS, COAGULANTS, AND OXIDANTS (WASTE WATER NOT PREFILTERED)

Treatment		COD of untreated, unfiltered, secondary effluent, mg/liter	COD after treatment, mg/liter
208 112	ppm Panther Creek Bentonite and ppm of $TiCl_4$	176	66
60 0.8 200	ppm $FeCl_3$, then ppm $Ca(OH)_2$; filtered through E + D 615 paper following agitation, then again treated with ppm Nuchar C-115	161	75
20 60 0.8 200	ppm $KMnO_4$, ppm $FeCl_3$, ppm $Ca(OH)_2$; mixture agitated, then filtered through E + D 615 paper; posttreated with ppm Nuchar C-115	149	52
20 400	ppm $KMnO_4$; agitated, filtered, then posttreated with ppm Nuchar C-115	149	56
450 8,060 4,600 6,800	ppm milled rutile in ppm H_2SO_4, plus ppm CaO (to precipitate acid-dissolved titanium), plus ppm Na_2CO_3 to neutralize treated mixture to pH 6.8	266	124
45 810 2,000 7,400 60 110	ppm milled rutile in ppm H_2SO_4, plus ppm $BaCO_3$, plus ppm Na_2CO_3 (to achieve alkalinity in mixture), then ppm $FeCl_3$ (final pH adjusted to 6.8 with additional ppm H_2SO_4)	266	137

placed in a medium with many is indeed a versatile material. This study is, however, concerned primarily with massive removal of refractory contaminants. Columnar-bed treatments,

Table 11. BATCH TREATMENTS EMPLOYING H_2O_2 AND IONAC A-540 ION EXCHANGE RESIN (Cl^- FORM)

Initial COD of sewage, mg/liter	H_2O_2 added, ppm	H_2O_2 contact time before resin treatment, min.	Resin, ppm	Residual COD, mg/liter
115	None	None	555	58
115	10	10	None	121
115	10	10	555	75
115	10	100	500	65

while relatively more time consuming than batch treatments, readily tell whether or not a material is capable of lowering the COD of a secondary effluent to zero. The flow rate in testing of most columnar-bed materials was 10 milliliters of effluent every 2 minutes.

ION EXCHANGE RESINS

Ionac A-300 and Ionac A-540

Two resin beds were set up in glass tubes having sintered-glass discs to support the resin. The inside diameter of these tubes was 23.5 millimeters. One bed consisted of 10.00 grams (dry weight) of Ionac A-300 (a granular, medium-base anion exchanger) and had a bed volume of 29.7 milliliters after soaking and washing with demineralized water. The other bed consisted of 10.00 grams (damp, swollen weight; 5.17 grams dry weight) of Ionac A-540 (a bead-type, strong-base anion exchanger), and had a bed volume of 16.95 milliliters. Both resins were in the chloride form. Filtered Mt. Holly effluent was passed through each at a rate of about 10 milliliters every 2 minutes. COD and chloride tests were run on the effluent after passage through the beds. The results of these tests versus the volume of effluent passed through each bed are summarized in Figures 8 and 9. The increase in COD and chloride content during the passage of the first 1,000 milliliters of effluent through the Ionac A-540 resin bed may be attributed to the fact that newly synthesized ion exchange resins often have a tendency to leach impurities when first placed into service. The breakthrough capacity of each of these resins appears to be about 100 bed volumes. Considerably more effluent than that was, however, passed through each. After the passage of the effluent through the beds, attempts were made to regenerate the resins to their original capacities

with warm (60°C), 10 percent NaCl solution followed by warm, 10 percent NaOH and then again by 10 percent NaCl. The A-300 was regenerated to about 14 percent of its original capacity,

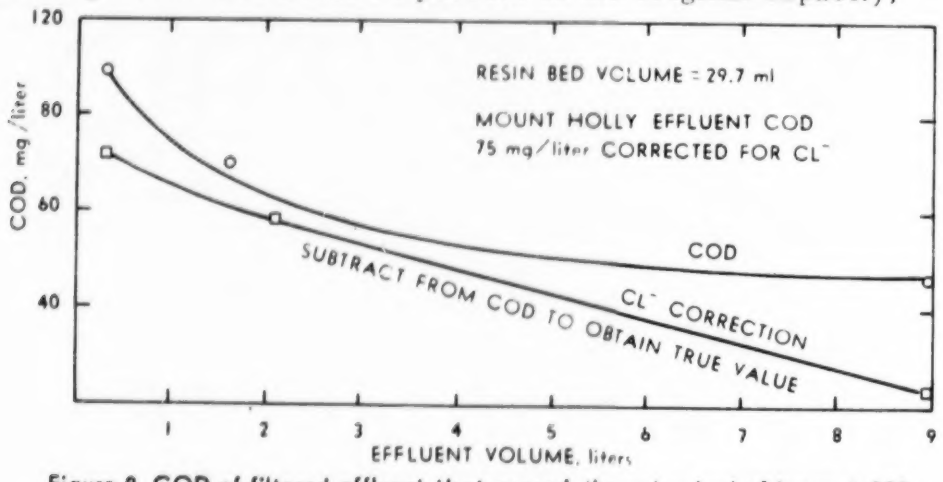


Figure 8. COD of filtered effluent that passed through a bed of Ionac A-300.

while the A-540 was regenerated to about 46 percent. This fouling might have been reduced if regeneration had been attempted sooner. From the data observed from these two runs, other

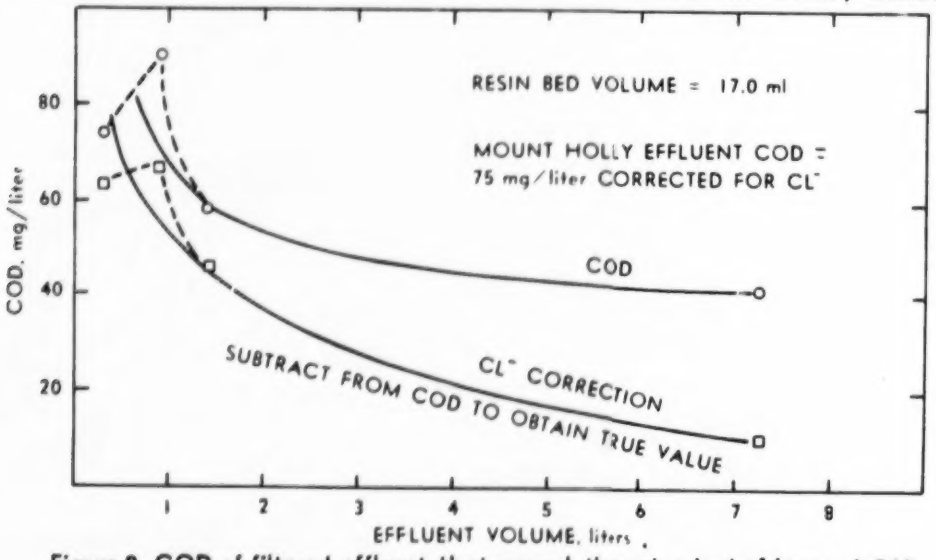


Figure 9. COD of filtered effluent that passed through a bed of Ionac A-540.

synthetic ion exchange resins were considered with regeneration following the passage of 100 bed volumes through the bed.

Ionac A-260

A 17.4-milliliter bed of Ionac A-260 (granular, weak-base anion exchanger) containing 5.0 grams of the resin (dry basis) was set up in a glass tube with a sintered-glass bottom. Prefiltered secondary effluent was then passed through this bed. After 20 bed volumes had passed through, the effluent so treated had dropped in COD by 40 milligrams per liter. After 100 bed volumes, the drop in COD was only 16 milligrams per liter. Attempts to regenerate this resin with NaCl and NaOH failed.

Ionac XLA-400

Two columnar beds of Ionac XLA-400 (a bed-type, strong-base anion exchanger) were employed in testing the ability of this resin to remove refractory contaminants from waste water. Each bed had a depth of 35 millimeters and a diameter of 23.5 millimeters (or a bed volume of 15.17 milliliters). The waste water was passed through the beds at a rate of 10 milliliters every 2 minutes. Bed No. 1 was initially eluted with a 10 percent aqueous NaCl solution to assure maximum chloride conversion and regenerated after each succeeding 100 bed volumes by successive treatment with aqueous solutions of 10 percent NaCl, 10 percent NaOH, and 10 percent NaCl. Bed No. 2 was also initially eluted with 10 percent NaCl solution, but was regenerated after 100 bed volumes with 10 percent NaCl followed by 0.5 percent aqueous NaOCl. Each bed was rinsed thoroughly with demineralized water after each regeneration treatment (to remove excess NaCl, NaOH, or NaOCl). The OH^- exchanged by the resin (of Bed No. 1) was quantitatively measured after its displacement by Cl^-. This test provided some measure of the regenerability of the resin in this bed.

Resin bed No. 1. A total of 5,047 milliliters of filtered effluent, whose COD varied from 72 to 137 milligrams per liter, was passed through this bed. Regeneration was attempted twice; after passage of 1,766 and 3,427 milliliters of the effluent through the bed. After the effluent passed through the column, its residual COD varied from 25 to 82 milligrams per liter. The drop in COD, after the effluent passed through the column, varied from 41 to 62 milligrams per liter. The chloride correction remained fairly constant, varying from 37 to 44 milligrams per liter. The constancy of the chloride corrections is an indication that the resin was being successfully regenerated. Further indication that the resin was successfully regenerated was found in the OH^- capacity of the resin after treatment with 10 percent NaCl. After the first regeneration, the bed had a capacity of 15.85 milliequivalents of NaOH, and after the second regeneration, 15.55.

Resin bed No. 2. A total of 3,156 milliliters of filtered effluent, varying in COD from 72 to 137 milligrams per liter, was passed through this bed, which was regenerated after 1,646 milliliters of effluent had passed through it. A comparison of the performance of Beds 1 and 2 is shown in Table 12.

Ionac XLA-400 resin (chloride form), 95-milliliter bed. In an effort to increase the drop in COD of secondary effluent in its passage through NaCl-regenerated Ionac XLA-400 resin, a larger bed was set up. It was felt that the drop in COD might be

increased by employing a larger bed, which would increase contact time and minimize the effects of channelling. Accordingly, a bed with a depth of 251 millimeters and a diameter of 22 milli-

Table 12. WASTE-WATER TREATMENT EMPLOYING 15-ml BEDS OF IONAC XLA-400

Quantity of waste water passed through bed (in bed volumes)		Influent COD, mg/liter	Effluent COD, mg/liter		Drop in COD after passing through bed, mg/liter	
Bed No. 1	Bed No. 2		Bed No. 1	Bed No. 2	Bed No. 1	Bed No. 2
21.4	-----	94	50	--	44	--
102	-----	87	25	--	62	--
116	0	Regenerated				
137	22.1	72	31	32	41	40
236	98.2	72	30	25	42	47
236	108	Regenerated				
343	198	137	82	59	55	78

meters (or a bed volume of 95 ml) was tried. The initial COD of the effluents passed through this bed varied from 99 to 125 milligrams per liter. The results of the testing done on this bed are summarized in Table 13.

Table 13. WASTE-WATER TREATMENT EMPLOYING A 95-ml BED OF IONAC XLA-400

Quantity of effluent passed through bed (in bed volumes)	Influent COD, mg/liter	Effluent COD, mg/liter	Drop in COD after passing through bed, mg/liter
3.63	99	28	71
6.63	125	24	101
15.08	122	52	70
21.83	122	41	81
31.58	117	49	68

When the values in Table 13 are compared with the drop in COD encountered with the smaller column (Bed No. 1, chloride form), the results indicate that the column efficiency can be increased markedly, at least for the number of bed volumes reported above, by the use of a longer column of resin.

Note that the properties of this resin can be modified according to degrees of cross-linking. These tests indicate that this resin is regenerable after the passage of waste water through it, in spite of the fact that such a condition is conducive to fouling. A sufficient number of cycles was not, however, recorded to establish that this resin would be an economical agent for refractory-contaminant removal from secondary effluent. If regeneration problems occur after several cycles, the ability to vary the degree of cross-linking within this resin might effect a solution to such problems.

Ionac C-270 and C-240 (H^+ forms)

Two commercial cation exchange resins were employed in columnar-bed testing procedures, primarily in the testing of Rosin Amine D, for removal of this Rosin from aqueous media.

Ionac C-270 (weak-acid resin) and C-240 (strong-acid resin) were used in these tests. Both were in the H^+ form. Three-hundred milliliters of a 50 ppm aqueous solution of Rosin Amine D were passed through a 15-milliliter bed of each of these resins. Prior to passage, the Rosin Amine D solution exhibited a COD of 154 milligrams per liter and readily formed a precipitate on the addition of a few drops of sulfuric acid. After passage through Ionac C-270, this solution had been lowered in COD to 18 milligrams per liter. After passage through the Ionac C-240 bed, this formerly 50 ppm solution had been lowered in COD to 9 milligrams per liter. The eluted liquor from each column was again tested with a few drops of sulfuric acid, and no precipitate was formed. No further testing was done on Ionac C-270.

Tests employing Ionac C-240 (H^+ form resin) were run to study further the effect of Rosin Amine D on prefiltered (Whatman No. 5 paper) secondary effluent, and the effect of Ionac C-240 on the effluent. Initial testing of this amine in batches had produced a treated effluent with a COD somewhat higher than the untreated effluent. Filtered Mt. Holly effluent, with a COD of 100 milligrams per liter, was employed.

Five-hundred milliliters of the effluent were treated with 50 ppm of Rosin Amine D, then filtered. One percent diatomite was employed in the filtration to effect reasonable clarification of the effluent after the amine treatment. Three hundred milliliters of the amine-treated, diatomite-filtered effluent was passed through a 15-milliliter bed on Ionac C-240 resin. The COD of the eluted effluent was 48 milligrams per liter.

A second 15-milliliter bed of the Ionac C-240 resin was used to treat 300 milliliters of the prefiltered secondary effluent that had a COD of 100 milligrams per liter. This portion was pretreated only with a 1 percent diatomite filtration. The effluent, after passing through an Ionac C-240 bed, had a COD of 66 milligrams per liter. The use of Rosin Amine D does not, therefore, appear promising. Its COD-lowering effect on the effluent was only 12 milligrams per liter.

PROTEINACEOUS MATERIALS

A few proteinaceous materials were tried, without modification, in attempts to lower the COD of secondary effluent. Prefiltered secondary effluent was passed through a bed of a 40 percent gluten feed supplement, a bed of casein, and a bed of

soya protein. In an effort to prevent dispersion of the protein, the pH of the effluents that passed through the casein and soya protein beds was preadjusted. Preliminary attempts were made to prevent agglomeration of proteins by mixing them with sand. No success was registered with the sand-protein mixture.

Forty Percent Gluten Feed Supplement

A bed of 40 percent gluten feed supplement was prepared. This bed was prerinsed with demineralized water until no further color was imparted to the rinse water. Prefiltered effluent was then passed through the column, whereupon the COD was greatly increased. A 50-milliliter portion of the eluted effluent consumed all the dichromate during the reflux period. A coagulation treatment of the eluted effluent with 60 ppm $FeCl_3$ was tried. This posttreatment failed to lower the COD to a point where a 50-milliliter portion would not reduce all the dichromate in the quantitative COD test.

Casein and Soya Protein

Columnar beds of both casein and soya protein were tried during this study. Preadjustment of the pH of the waste water to 3.0 with HCl was employed, prior to passage through these beds, in an effort to prevent agglomeration and leaching. No success was attained.

MODIFIED PROTEINACEOUS MATERIALS[6, 7*]

Various attempts were made to modify proteins so that they could be tested in bed form. Modification treatments were tried wherein proteins were (1) dispersed in NaOH solution, then reacted with a ferric compound; (2) reacted with a ferric compound in a granular, undispersed state; (3) reacted with formaldehyde in the undispersed state; (4) reacted with formaldehyde in the undispersed state, then with a ferric compound, an acid, an acid salt, or a base; and (5) reacted with formaldehyde in the dispersed state, then with a ferric compound.

During the quest for suitable proteins and modification techniques, two groups of rather elementary tests employing zein and casein compounds were set up. The tests were intended to furnish information to be used in coping with the problem of leaching. Both groups consisted of proteinaceous materials in contact with waste-water effluent for 65 hours, but with one group, the pH of the waste water was preadjusted to 3.0 with 1:1 HCl. None of the proteinaceous materials imparted any noteworthy immediate changes in the appearance or odor of the supernatant waste water. The appearance and odor of each mixture were noted

---

*A copy of U.S. Pat. 2,393,269 is in Appendix A of this report.

again after the contact period. The results of these tests are given in Table 14.

Table 14. SOME EFFECTS OF WASTE WATER ON CASEIN AND ZEIN, AS MODIFIED (FILTERED WASTE WATER WITH NO PREADJUSTMENT OF pH)

Proteinaceous materials	Observations after 65 hours' contact time
None (control)	Typical appearance and odor
Undispersed zein treated with $FeCl_3$	No change in appearance; odor of protein is noticeable
Casein treated with NaCl and formaldehyde	No change in appearance; very slight odor of waste water, but not as strong as control
Zein treated with NaCl, formaldehyde, and H_2SO_4	Somewhat cloudy on shaking; slight odor of protein
Zein alone	Clear on shaking; rather strong protein odor; slight putrid odor also detected
FILTERED WASTE WATER WITH pH PREADJUSTED TO 3.0	
None (control)	Typical appearance and odor (unchanged by adjustment of pH)
Undispersed casein treated with $FeCl_3$	No change in appearance; odor of protein noticeable
Casein treated with NaCl and formaldehyde	No change in appearance; very slight odor of waste water, but not as strong as control
Zein treated with NaCl, formaldehyde, and H_2SO_4	Clear on shaking; very slight protein and waste-water odors
Zein alone	Cloudy on shaking; strong putrid odor

Reaction of Dispersed Proteins With Ferric Compounds

Of the proteins that were dispersed in caustic then precipitated with a ferric compound, only casein showed promise. The other materials (Permutit 65 gelatin, Swift's "Fluid 69," Swift's "4V," and ADM Soya Protein "Adpro 112 B"), when dispersed in 2 percent NaOH on the weight of the protein and precipitated with 10 percent $FeCl_3$ on the weight of the protein, were not amenable to bed-testing procedures.

Similarly dispersed casein was reacted with $Fe_2(SO_4)_3$. The resulting curds were mixed with washed sand, and the mixture was tested as a bed material. Prefiltered secondary effluent readily passed through this bed at a relatively unrestricted flow rate. Prior to passage through the bed, the waste water had a COD of 110 milligrams per liter. After passing through the bed, a portion of the waste water was reduced in COD to 76 milligrams per liter. The COD of the effluent from this bed was further reduced to 57 ppm by coagulating it with 60 ppm $Fe_2(SO_4)_3$ calculated as $FeCl_3$. The additional drop in COD was attributed to the coagulation of protein, which had leached from the curdy casein precipitate.

Reaction of Undispersed Proteins with Ferric Compounds

Several undispersed, proteinaceous materials, reacted with ferric chloride or ferric sulfate, were employed in these studies. Casein, 40 percent gluten feed supplement, food grade (70%) gluten, soya protein, and various glues and gelatins were reacted with ferric chloride. The resulting glue and gelatin compounds exhibited no appreciable stability when in contact with water or waste water. Eventually all these compounds were abandoned after various stages of testing, owing to their leaching of organic materials, even when 20 ppm of NaOCl was added to the effluent to control microbes.

The less hydrophilic of these compounds, notably the 40 percent gluten feed reacted with $FeCl_3$, proved, however, to have an affinity for ABS. A test employing a synthetic laundromat effluent containing 60 ppm ABS was run on a columnar bed of this compound. The material used in this test was prepared as follows: 30.0 grams of 40 percent gluten feed supplement (GLF) was reacted with an excess of $FeCl_3$. The material was rinsed twice during which time 3.9 grams (dry basis) of fine material was removed and discarded. It was estimated that the feed would react with approximately 4 percent of its weight in $FeCl_3$.

The results of the analysis of the effluent after it had passed through this bed are shown in Table 15.

Reaction of Proteins with Formaldehyde

Granular, undispersed casein was reacted with formaldehyde. Thirty-four grams of casein was placed in a solution consisting of 54 grams of NaCl, 60 milliliters of 37 percent formaldehyde, and 400 milliliters of demineralized water. The mixture was held at 60°C for 15 minutes, with occasional stirring, then the supernatant solution was decanted, and the treated casein was washed free of NaCl and formaldehyde. It is believed that the

NaCl-formaldehyde solution can be re-used several times to "harden" proteins.

Table 15. EFFECT OF A GLUTEN FEED-$FeCl_3$ COMPOUND ON THE ABS IN SYNTHETIC LAUNDROMAT EFFLUENT CONTAINING 60 ppm ABS

Cumulative volume of effluent passed through bed, ml	ABS content of effluent passed through column, ppm
800	None found
3,100	2.5
3,800	3.6
4,750	4.8
9,000	13.6[a]

[a]Composite of final 4,250 ml passed through column.

An attempt was made to repeat the procedure with 50 grams of zein. The zein coagulated into a single, sticky, elastic lump. This lump was hardened by addition of 10 milliliters of concentrated H_2SO_4 to the bath solution followed by oven drying at 100°C. Air was squeezed out of the lump during the sulfuric acid treatment to allow penetration of H_2SO_4. Owing to the questionable uniformity of this material, it was not tested for its capacity to remove refractory contaminants from waste water. No further attempt was made to devise a method of obtaining a uniformly cross-linked and hardened zein product, owing to the cost of zein as compared with the cost of casein.

The same procedure employed to harden casein by NaCl and formaldehyde was also successfully employed to harden a relatively cheap livestock feed mixture containing 40 percent corn gluten protein.

The protein-formaldehyde compound proved to have no affinity for the organic refractory contaminants in waste water. The casein-formaldehyde compound proved capable, however, of separating metal salts in an aqueous mixture. Color bands, characteristic of the color imparted by certain cobalt, iron, chromium, and copper salts, appeared in a bed of casein-formaldehyde compound when a mixture of these salts was eluted through that bed.

Further reaction of the casein-formaldehyde compound with ferric compounds showed much promise for removal of refractory contaminants from waste water. As a result, the formulation and testing of many variations of protein-formaldehyde-acid and acid salt compounds were given much attention during this study.

A hypothesis was proposed to account for the failure of the formaldehyde-treated casein, by itself, to remove any organic matter from the water and for the ability of the protein to do so after contact with strong ferric chloride or ferric sulfate solutions. We believe the mechanism can be explained as follows:

(a) Low pH of the iron salt solution promotes hydrolysis of methylol groups, which block the amino exchange sites on the protein.
(b) Low pH also promotes the splitting of inner salt bridges (the so-called zwitterion), which exposes more amino exchange sites.

Partial corroboration of this hypothesis was obtained when the formaldehyde-treated casein was exposed for some hours to hydrochloric acid. Thus when a sample of Mt. Holly secondary effluent that had a COD of 107.7 milligrams per liter was passed through a bed of casein-formaldehyde-hydrochloride, its COD was lowered to 30.7 milligrams per liter at the seven-bed volume point. The eluate was moderately strongly acidic (2.5 to 3.5 pH) and ran high in chloride. Less successful were sulfuric and phosphoric acids, even though phosphoric acids were to have the additional virtue of easy phosphate removal per calcite bed.

The lime treatment of the formaldehyde protein was based on the premise that sufficient hydrolysis of zwitterion and methylol groups could be induced to dispense with chloride completely. The results indicate that a severe leaching of protein takes place so that the eluate displays a somewhat higher COD than the raw influent.

Reaction of Undispersed and Dispersed Protein with Formaldehyde plus Various Other Compounds

Granulated, undispersed casein was reacted with formaldehyde, then with an excess of ferric chloride. This material was employed as a bed for testing its effect on the refractory contaminants in secondary effluent.

This bed had a depth of about 78 millimeters and a volume of about 30 milliliters. Filtered effluent was passed through this bed until it no longer lowered the COD of the effluent. Table 16 summarizes the results of the passage of the effluent through this bed.

After exhaustion with secondary effluent, this bed was regenerated as follows:

(a) The Fe^{+++} was first eluted with 40 milliliters of 9 percent HCl solution, then the excess HCl was washed out with demineralized water.

(b) The adsorbed organic materials, apparently now more loosely bound in or on the casein compound in the absence of Fe^{+++}, were eluted with 100 milliliters of 9 percent NH_3. The excess NH_3 was then washed out with demineralized water.

(c) Finally 6 percent $FeCl_3$ was passed through a bed of casein compound until original volume and color were returned.

Table 16. TREATMENT OF SECONDARY EFFLUENT WITH A CASEIN-FORMALDEHYDE-$FeCl_3$ COMPOUND

Quantity of waste water passed through bed (in bed volumes)	Initial COD of effluent, mg/liter	COD of effluent after passing through bed, mg/liter	Drop in COD, mg/liter
5.87	105	45	60
15.80	105	60	45
29.80	100	97	3

After regeneration, a 60 ppm solution of standard ABS was passed through the bed. The regenerated bed successfully removed all ABS from the solution. More than 11 bed volumes of the solution were passed through the bed.

Another bed, with the same depth and volume as the casein compound described above, was set up. This bed consisted of a formaldehyde-hardened livestock feed mixture (40% corn gluten) reacted with an excess of $FeCl_3$. After about 15 bed volumes of 60 ppm ABS solution were passed through the bed, the ABS in the effluent was still being lowered to less than 0.1 ppm.

Leaching of COD-imparting organic materials by this feed-formaldehyde-$FeCl_3$ compound impeded the evaluation of its effect on waste water. Another bed of this material was, however, set up to learn what effect it would have on the color bodies in Rancocas Creek water. Much of this coloring matter is attributed to humates and humic acids; similar materials are present in waste water.

The creek water was first filtered through Whatman No. 5 paper and then passed through the column. While this test was not intended to be quantitative, it indicated that the bed material will remove much of the material responsible for imparting color to the creek water.

Two more beds of casein-formaldehyde-$FeCl_3$ compound were set up. Filtered Mt. Holly waste water was passed through one, and filtered Camden waste water was passed through the other. Both columns were exhausted after approximately 43

bed volumes had passed through. The initial COD of each effluent was similar (Mt. Holly = 80 to 86, Camden = 69 to 80 mg/liter). The waste water passed through each column was lowered similarly in COD (Mt. Holly by 6 to 43, Camden by 11 to 38 mg/liter). The apparently greater capacity of the casein-formaldehyde-$FeCl_3$ compound for COD-imparting materials in these examples (as evidenced by the 43 bed volumes) as compared with the example given above (29.8 bed volumes) is probably attributable to two factors. One is, of course, the difference in COD between the original effluents (69 to 86 versus 100 to 105). The other is the formulation of the compound. Longer contact times with formaldehyde and $FeCl_3$ seem to enhance the affinity of the casein compound for the refractory contaminants; the compound used in the two beds to compare Mt. Holly with Camden effluents (Table 17) had longer reaction times. The contact time with formaldehyde was 1 hour and 15 minutes at 60°C versus the usual 15 minutes at 60°C. The contact time with $FeCl_3$ was 4 hours versus the usual 1 to 2 hours.

Table 17. COMPARISON OF MT. HOLLY VERSUS CAMDEN SECONDARY EFFLUENTS (COLUMNAR-BED TREATMENTS WITH CASEIN-FORMALDEHYDE-$FeCl_3$ COMPOUND)

Mt. Holly effluent				Camden effluent			
Bed volumes	Initial COD, mg/liter	COD after treatment, mg/liter	COD-lowering effect, mg/liter	Bed volumes	Initial COD, mg/liter	COD after treatment, mg/liter	COD-lowering effect, mg/liter
6.9	80	46	34	7.35	75	48	27
17.8	83	56	27	17.7	69	31	38
34.5	85	42	43	34.5	80	56	24
43.6	86	80	6	44.0	70	59	11

Formulating and testing of other casein-formaldehyde compounds was undertaken. The compounds, and their effect on waste water, as compared with that of casein-formaldehyde-$FeCl_3$ compound are summarized in Table 18.

Several other formulations of the casein-formaldehyde compound with additional agents were prepared and tested in granular, in granular-semifloc, and in floc forms to determine their effects on the refractory materials in secondary effluent. Emphasis was placed on the control of soluble by-products of the treatments.

These casein compounds were subjected to lengthy rinses with very large volumes of water, and the rinse water was tested to determine its COD. This was done to predissolve any soluble organic matter from the product prior to its use in treatment of waste water. Another possible source of leachable organic materials could come from microbial action on the casein

compound. While the casein, when hardened with formaldehyde and treated with a ferric iron compound, is resistant to such attack, it is believed that as the material exchanges refractory

Table 18. COMPARISON OF EFFECTS OF SOME MODIFIED CASEIN COMPOUNDS ON REFRACTORY CONTAMINANTS IN WASTE WATER

Casein-formaldehyde	Capacity, compared with casein-formaldehyde-$FeCl_3$
-$Fe_2(SO_4)_3$	Somewhat greater
-$Al_2(SO_4)_3$	Removes organic materials, but results are not conclusive, since bed was not exhausted; probably equal to or less
-HCl	Removes organic materials, but results are not conclusive, since bed was not exhausted; probably greater
-H_3PO_4	Less
-H_2SO_4	Less
-$Ca(OH)_2$	Less

contaminants for acid components of the compound, local pH-raising effects could permit bacterial action simultaneously with exchange of refractory contaminants at other sites. Mt. Holly's secondary effluent is chlorinated as a safety measure to control pathogens owing to the limited size of the Rancocas Creek, into which the final effluent is ejected. This amount of residual chlorine may well be insufficient to protect the casein compound until exhausted.

Another way in which soluble materials are imparted into the treated effluent is by their exchange for the organic refractory contaminants in the effluent. These soluble materials are inorganic acids. Which acid will be present is, of course, determined by the acid or acid salt component of the casein compound. H_3PO_4 can be removed via a calcite bed. The more promising forms of the casein compound are, however, the $FeCl_3$ form, the $Fe_2(SO_4)3$ form, and the HCl form. Their use would necessitate the removal of relatively large quantities of HCl or H_2SO_4. We have estimated that Ionac A-260 resin can solve this problem. The cost of this additional treatment with A-260 will vary somewhat according to whether its use is for HCl or H_2SO_4 removal. The ultimate cost of the use of this resin will depend on the

organic content of the effluent after treatment with the casein compound, because of the possibility of organic fouling. This phenomenon can probably be eliminated by a polishing step, wherein activated carbon might be employed. The possible use of this resin in a posttreatment, deacidifying step will be discussed later in more detail.

The formulation and testing of casein-formaldehyde compound with additional agents, prepared to emphasize control of organic leaching, was as follows:

(a) An attempt was made to eliminate the Cl^- ion from treated waste water by treating a casein-formaldehyde-iron chloride compound with calcium oxide (1 gram of CaO: 30 grams of casein compound) to displace Cl^- with OH^-. This proved unsatisfactory. This was followed by two attempts to achieve the desired result by use of NaOH. A 0.1 normal NaOH solution had very little effect, while a 10 percent NaOH solution displaced the Cl^-, but rendered the compound more prone to leaching of organic materials.

(b) Another attempt was made to solve the Cl^- ion problem by trying to pick it up in a bed of casein-formaldehyde compound. This bed was used to posttreat waste water passed through a bed of casein-formaldehyde-hydrochloric acid compound. When the first bed became exhausted, the second bed was to have been activated by the HCl picked up during the treatment process. It was determined from this and other tests that casein-formaldehyde compounds have little or no affinity for HCl at the concentrations involved here.[8]

(c) Casein was reacted with HCl, with $CaCl_2$, and with $Ca(OH)_2$. The resulting compounds each proved to be unsatisfactory. This was apparent when excessive foaming of the rinse water was noted. They were given the advantage of several water rinses, but still failed to be useful in the treatment of secondary effluent. Additional chlorination of the waste water was tried, in the case of the casein-$Ca(OH)_2$ compound, but did not help. Casein-calcium hydroxide compound was prepared and hardened with formaldehyde. This material also proved to be of no value in removing refractory contaminants from waste water.

(d) A casein-formaldehyde-hydrochloric acid compound was treated with 3.5 percent NaOH solution, rinsed, and retreated with 1.5 percent NaOH solution. The resulting compound was apparently relatively chloride-free. As in the case of the previously mentioned NaOH treatment of casein-formaldehyde-iron chloride compound, (a) above, the chloride was eliminated in the treated

GPO 812-253-5

effluent. The compound was, however, rendered more prone to the leaching of organic materials. The above formulation was repeated, with a 10 percent $NaNO_3$ solution treatment followed by a 5 percent NaHCO solution treatment in place of the NaOH treatments. Again in the compound proved unsatisfactory, owing to leaching of organics.

(e) The leachable organic materials in the casein compounds are probably proteins or protein fragments that might be rendered insoluble or more stable, or both, if cross-linked with a molecule larger than formaldehyde. Dialdehyde starch was, therefore, used in one experiment to replace formaldehyde. Although this formulation removed refractory contaminants from secondary effluent, it apparently did not offer a solution to the problem. Since the cross-linking agent represents a relatively small portion of the cost of modified casein compound, more expensive agents can be considered for this purpose. This is particularly true if they are more efficient than formaldehyde, which forms several condensation products with casein other than the desired intermolecular, cross-linked product. These products must then be hydrolyzed by water rinse.

(f) Casein dispersed in NaOH solution (0.5% NaOH on the weight of the casein) was precipitated with hydrochloric acid in the form of a floc, then reacted with formaldehyde, then with iron chloride. The purpose here was to try to eliminate leachable materials during reprecipitation of the casein and also to increase capacity for refractory contaminants by increasing the surface area of the compound. This material was also given the advantage of lengthy rinses with water. When compared with casein-formaldehyde-iron chloride on a weight basis, this compound appears to have a superior capacity for refractory contaminants. It is not, however, as stable against the effects of microbes when allowed to stand for a period of several hours.

(g) Water soaking of casein, prior to reaction with formaldehyde and iron chloride, was tried as an alternative to reprecipitation of the casein for preremoval of soluble organic contaminants. One-hundred grams of casein was soaked in 1 liter of water at room temperature for 2 hours. Medium agitation was maintained during this period at a rate that was not so slow as to permit aggregating of the semisolid casein granules, nor so fast as to effect complete solution of the granules. After two rinses of the casein, during which great losses occurred, the soft granules were reacted with formaldehyde, then with ferric chloride. The resulting

compound was rinsed with 2 liters of water. Tests of the material for leaching and affinity for refractory contaminants of waste water were encouraging, but the dissolution of the casein during presoaking results in too great a loss for the process to be economical, unless the casein so dissolved or dispersed could be used for another purpose.

INORGANIC AND TREATED INORGANIC MATERIALS

Calcined, Diatomaceous Earth

A bed of a commercial, granular-form, calcined, diatomaceous earth was tried in an effort to remove refractory contaminants from filtered waste water. This material proved unsatisfactory. Bed testing was abandoned because of a progressive restriction of the flow rate, which occurred during testing.

Inorganic Materials Treated with Rosin Amine D Acetate

Rosin Amine D acetate solution (500 ppm) was used to treat Ionac C-100 (a synthetic zeolite), Hyflo Super-Cel (a diatomite), and Dicalites 416, 436, 4106, and 4156 (various particle size gradients of perlite).

Three-hundred milliliters of filtered waste water was passed through a prerinsed, 15-milliliter bed of each of the treated Ionac C-190 and Hyflo Super-Cel, and discarded. An additional 70 millilitèrs was eluted and tested for COD. Initially, the COD of the prefiltered effluent was 100 milligrams per liter. After the effluent passed through the treated Ionac C-150 bed, its COD was 102 milligrams per liter, and after it passed through the treated Hyflo Super-Cel bed, its COD was 94 milligrams per liter.

While treated perlite performed no better on waste water this material removed the ABS from a synthetic laundromat effluent that had an original ABS concentration of 60 ppm.

ACTIVATED CARBON

A 190-milliliter bed of Ionac P-50 granular, activated carbon (91 grams) was employed as a posttreatment of prefiltered secondary effluent. The pretreatment was a batch coagulation, at pH 3.0, employing 75 ppm of gluten (food grade) and 45 ppm of $FeCl_3$. The pH adjustment was made with HCl.

The prefiltered effluent used in this test had an initial COD of 98 milligrams per liter. The gluten-$FeCl_3$ treatment lowered the COD to 64 milligrams per liter. A similar coagulation treatment employing 200 ppm gluten and 120 ppm $FeCl_3$ lowered the COD of a portion of the same initial effluent to 51 milligrams

per liter. The COD of this treated effluent, when the larger dosages were used, was not further lowered on neutralization to pH 6.5 with CaO. The coagulant-treated effluents, with a COD of 64 milligrams per liter, was then passed through the carbon column. The first 400 milliliters eluted was discarded. A COD test was run on the next 100 milliliters eluted and found to be zero. This eluant was approximately neutral in pH, and no chlorides were present. This phenomenon may be attributable to a small mineral fraction in the carbon and may indicate serious competition between the HCl and organic matter for adsorption sites on and within the carbon granules.

A portion of the effluent, which was coagulated with 75 ppm gluten and 45 ppm $FeCl_3$ but not passed through the carbon column, was neutralized to pH 6.5 with CaO. The effluent's COD, after this neutralization step, was further lowered from 64 to 52 milligrams per liter. In contemplating further post-treatment (of coagulated-carbon-polished effluent) with Ionac A-260 to remove acid, this CaO neutralization step cannot, however, be considered.

A second 190-milliliter bed of Ionac P-50 granular, activated carbon was employed to treat prefiltered secondary effluent. The initial COD of this effluent was 106 milligrams per liter. The first 550 milliliters eluted was discarded, and then 3,450 milliliters more was passed through. The COD of this amount of eluted effluent was 41 milligrams per liter.

A third 190-milliliter column of Ionac P-50 granular, activated carbon was again used to test its affinity for the refractory contaminants in filtered secondary effluent. The initial COD of the effluent used in this test was 100 milligrams per liter. After 1,410 milliliters was passed through this bed, the COD of the eluted effluent was zero. The next 85 milliliters eluted had a COD of 9 milligrams per liter. After a total of 2,005 milliliters of the effluent was eluted, an additional 250-milliliter portion was eluted and tested for COD. The COD of this last 250-milliliter "cut" was 15 milligrams per liter. The total volume of effluent eluted through this third carbon column was 2,255 milliliters.

Sludge Blanket Testing

A Spaulding-type, laboratory bench model precipitator was set up (Figure 4), and about 100 grams (dry basis) of a casein-$FeCl_3$ floc was placed in it. The casein-ferric chloride floc was prepared by dispersing casein in NaOH solution (0.5% NaOH on the weight of the casein), then adding the $FeCl_3$ as a 10 percent solution. This material was tested in a modified, laboratory scale, sludge blanket apparatus. Thirty ppm of NaOCl was added to the effluent to afford additional protection of the bed. Since the floc is known to have an affinity for refractory

contaminants in waste water, this experiment was intended as a preliminary test to gain knowledge of the behavior of the floc under continuous upflow conditions involving some of the principles of the sludge blanket apparatus. The material was not entirely satisfactory from this standpoint. Channelling was visually obvious, but was controlled by shaking the jug occasionally. This disturbed the floc bed sufficiently to require post-filtering of the effluent, since addition of clays at this point did not materially affect the settling properties of the solids. After about 4,500 milliliters of effluent had passed through the bed, the COD of the resulting effluent was lowered from 86 to 38 milligrams per liter.

The sludge blanket apparatus was modified by incorporating the basic design features of the Permutit Precipitator. It consisted of an agitator down through the stem of a long-stem, inverted funnel, which had been placed in a 4-liter beaker. The effluent was passed downward through the stem and upward through the narrow, circular opening between the perimeter of the funnel and the side walls of the 4-liter beaker (close to the bottom of the beaker). The sludge blanket buildup takes place outside the funnel, and above the narrow, circular opening.

Sufficient agitation (at 160 rpm) in the lower zone of the beaker is maintained in this way to minimize channelling through the sludge and permit a clarified, floc-free, quiescent upper zone. The addition of 30 ppm NaOCl to effluent used in sludge blanket treatment was continued.

The following "sludge blanket" treatments were done on filtered secondary effluent in the inverted funnel apparatus (30 ppm of NaOCl was added to all effluent):

(a) A casein-$FeCl_3$-formaldehyde floc (51 g dry basis) was prepared. Excess moisture was removed from the floc by vacuum filtration. The material was then placed in the apparatus, and filtered effluent with an initial COD of 98 milligrams per liter was passed through it. Then 4,000 milliliters was passed through the floc to fill the beaker, and an additional volume of 1,400 milliliters was passed through, and then a sample was taken for a COD test. At this stage, the COD was 29 milligrams per liter lower than that of the influent waste water. An additional 1,400 milliliters was passed through the sludge blanket, then a sample was again tested for COD. The COD at this point was 26 milligrams per liter lower than that of the influent waste water.

(b) An in situ precipitation of casein by an H_2SO_4-$Fe_2(SO_4)_3$ mixture was effected on a continuous basis in the sludge blanket apparatus. A total of 6 liters of filtered sewage with an initial COD of 98 milligrams per liter was

treated in this manner with 50 ppm casein and 30 ppm $Fe_2(SO_4)_3$. Both 14.4 milliliters of 5 percent H_2SO_4 and 0.38 gram of $Fe_2(SO_4)_3$ (72%) were premixed with 600 milliliters of the effluent. Then 0.33 gram of casein (90%) was dispersed in 0.1 normal NaOH solution and added to the remaining 5,400 milliliters of effluent. The mixtures were then blended in the sludge blanket apparatus, with the flow of the 5,400 milliliters of effluent containing casein regulated at approximately 10 times the flow rate of the 600 milliliters of effluent containing the acid and Fe^{+++} compound. The floc was permitted to build up as it formed. After this treatment, the COD of the 6 liters of effluent had been lowered by 25 milligrams per liter. The pH of the effluent so treated was lowered from 7.4 to 3.0.

(c) The in situ precipitation of casein was repeated with HCl and $FeCl_3$ in the place of H_2SO_4 and $Fe_2(SO_4)_3$. The same dosages (50 ppm casein and 30 ppm of the Fe^{+++} compound) were employed. This treatment lowered the COD of the filtered effluent (initially 87 mg/liter) by 29 milligrams per liter. The pH of the effluent after this treatment was 3.3. Addition of 60 ppm $FeCl_3$ as a posttreatment, followed by neutralization to pH 6.0 with CaO, did not further lower the COD of the effluent appreciably.

(d) $TiCl_4$ was next tested in the sludge blanket apparatus. Here, a rapid mixing chamber was added to the apparatus to allow continuous feeding and mixing of the $TiCl_4$ and the effluent. $TiCl_4$ is a fuming liquid that is difficult to handle and weigh. This problem was overcome by drawing a sufficient amount of the compound into a microburet by suction. The weight to be added was calculated as volume (in ml) according to its specific gravity. The microburet was attached to a capillary tube, which was fitted to a plastic bottle, whose bottom had been removed. This bottle projected beneath the surface of the effluent with which the $TiCl_4$ was to be mixed. The $TiCl_4$ was fed dropwise, from the capillary tube, through the airspace within the bottle, into the swirling filtered effluent, which initially had a COD of 89 milligrams per liter. When 140 ppm of $TiCl_4$ was employed on the weight of effluent, the treatment lowered the COD of the effluent by 40 milligrams per liter.

(e) Continuous coprecipitation of casein and $TiCl_4$ in the filtered effluent was also done in the sludge blanket apparatus. Then, 50 ppm of casein was placed in the effuent, the effluent and $TiCl_4$ (140 ppm) were fed into the mixing chamber (as were the $TiCl_4$ and effluent in the previous run). The pH of the effluent so treated

was lowered to 3.0 with HCl, then raised to 6.5 with CaO. This combination treatment reduced the COD of the effluent (initially 121 mg/liter) by 49 milligrams per liter.

Regeneration and Cost Estimate Studies

COST STUDIES: SOLID ADSORBENTS, COAGULANTS

Because of the marginal affinity of the ground minerals and industrial by-products for adsorbing organic materials from waste water, no emphasis was placed on a cost analysis of large-scale treatment with these materials. Some may prove useful in treatment of some trade and other waste waters. Morris and Weber[9] have found that activated aluminum oxide has an ABS uptake about one-third that of activated carbon. When these investigators extended these experiments to phenols and nitrochlorobenzenes, however, the results were not comparable to the results of their work on ABS. These investigators state that "It appears that this activated aluminum oxide does not have sufficiently broad adsorptive properties for general use, although it may be suitable for special treatment of detergent-bearing wastes."

Cost studies were undertaken for some coagulation techniques and for the preparation of a modified, granular casein compound. Regeneration of the compound was undertaken to gain information on costs as indicated by the amount of regenerants used and the loss in affinity for organic refractories following several regenerations.

In batch treatments (as a coagulant), casein will remove from waste water a greater percentage of its weight in the oxygen equivalent of organic refractory contaminants than will activated carbon. Carbon, through 20 regeneration cycles, can be expected to remove slightly more than its own weight in the oxygen equivalent of refractory contaminants. Here, the cost of 20 regenerations must be added to the initial cost of the carbon. Casein (at 19¢/lb versus about 15¢/lb for activated carbon) should be more economical (if regenerated only a few times) than carbon when employed in the sludge blanket, continuous-coagulation process. This process may not, however, remove all the refractory contaminants, and a polishing step using activated carbon may be required after the coagulation and sludge blanket treatments.

The cost of materials fed into the precipitator would be 13.1 cents per pound. This is based on current market figures for inedible casein, 19 cents; $FeCl_3$, 4 cents; and NaOH, 3 cents per pound. Dosages would be determined according to the

organic content of the liquor to be treated. Table 19 lists some applicable dosages together with treatment costs without regeneration of the sludge.

Table 19. RAW MATERIAL COSTS IN CASEIN-$FeCl_3$ COAGULATION TREATMENTS OF SECONDARY EFFLUENT

Additives, ppm	$/1,000 gal
Casein, 25, $FeCl_3$, 15	$0.0446
Casein, 50, $FeCl_3$, 30	$0.0892
Casein, 100, $FeCl_3$, 60	$0.1784

Table 19 includes the sodium hydroxide for the initial dispersion of the protein but omits the cost of prechlorination that would be required to inhibit microbial attack on the sludge blanket.

Considerably lower treatment costs can be realized if 70 percent gluten, food grade, at about $0.08 per pound is substituted for the inedible casein, at about $0.19 per pound. This will hold true, even though in dispersing the gluten, somewhat more NaOH would be required.

Regeneration of the casein-$FeCl_3$ floc was not attempted. A dilute acid rinse should, however, return this material to a form comparable to the raw casein used to prepare the original caustic dispersion.

The ferric compound (for example, in any protein-$FeCl_3$ treatment) makes a major contribution to the removal of organic refractory contaminants. The extra cost of adding from 167 to 233 percent protein, on the weight of the ferric compound, may not be justified in all cases and with all effluents (when the drop in COD due to a protein-ferric compound coagulation is compared with the drop in COD of a coagulation employing the ferric compound in the absence of protein).

In the lower dosages, for example, 25 ppm of casein to 15 ppm of $FeCl_3$, the use of protein as a coagulant could prove useful owing to proportionally greater synergistic effects at lower dosage levels. Moreover, in this dosage range, less Cl^- ion will be liberated, and Cl^- ion must only be removed at additional expense in a posttreatment. The latter statement may not, however, prove accurate owing to pH adjustments that must be made to effect coagulation (unless an acid such as H_3PO_4, which is readily removed by a calcite column can be substituted for HCl or H_2SO_4 in making these pH changes). That is, the pH of the

mixture must be reduced to about 3.0 in the course of the coagulation, and $FeCl_3$ at the more modest dosage levels will not in itself effect reduction of the pH to 3.0.

The cost of the sulfuric acid required to lower the pH of a mixture of 30 ppm $FeCl_3$, or $Fe_2(SO_4)_3$ calculated as $FeCl_3$, in secondary effluent to 3.0 is approximately $0.02 per 1,000 gallons. If hydrochloric acid is used instead of sulfuric, the cost will be $0.0372 per 1,000 gallons.

Consideration of the cost of $FeCl_3$, $Fe_2(SO_4)_3$, and $TiCl_4$ to treat 1,000 gallons of secondary effluent is given in Table 20. The amounts given are the costs of the metal salts only.

Table 20. COST OF SOME METAL SALT COAGULANTS IN TREATMENT OF 1,000 GALLONS OF SECONDARY EFFLUENT

Dosage, ppm	$FeCl_3$	$Fe_2(SO_4)_3$[a]	$TiCl_4$
15	$0.005	$0.0026	
30	0.010	0.0052	
60	0.02	0.0104	
90	0.03	0.0156	
120	0.04	0.0208	
140			$0.2332

[a]Dosage calculated as $FeCl_3$. Requires heat or extended contact time to effect solution. Cost of heating is not included in these figures.

COST STUDIES, BED MATERIALS

A bed-type compound of casein, formaldehyde, and ferric chloride was prepared for the sake of material balance and cost estimate. The cost of the casein, formaldehyde, and ferric chloride required to make 1 pound of this material is 21.6 cents, dry basis, allowing for losses in manufacture. This figure does not include the cost of sodium chloride (used as a catalyst in the formaldehyde treatment) or overhead costs of manufacture.

Studies of the feasibility of the regeneration of modified casein compounds indicated that this could be accomplished by a three-step process, as indicated earlier. In the case of a casein-formaldehyde-HCl compound, the elution of the Fe^{+++} (the first step) would be omitted.

A bed of casein-formaldehyde-ferric chloride compound was exhausted of its capacity for refractory contaminants in waste water. It was then stored at room temperature for 2 weeks, during which time the supernatant phase putrefied. It is believed that this was owing partly to the fact that a leachable portion of the protein was imparted into the supernatant phase and underwent microbial decomposition, and partly to attack on the protein compound itself (local pH effects would be neutralized on exhaustion, which would permit such microbial attack).

After the storage period, the bed was thoroughly rinsed, and regenerated six more times, during which no loss in bed volume was detected. No effluent was passed through the bed during these six regeneration cycles.

After the regeneration series, 3.1 bed volumes of filtered secondary effluent (Mt. Holly) were passed through the bed. This effluent was then discarded and 0.6 bed volume of the effluent through the column was collected and tested for COD and Cl^-. The net COD of the effluent (Cl^- corrected), prior to passage through the column, was 76.0 milligrams per liter. After passage of a total of 3.7 bed volumes of the sewage through the column, the net COD of the effluent was lowered to 16.9 milligrams per liter--a drop of 59.

The cost of regeneration solutions, exclusive of overhead costs of preparation and application of the solutions, would be approximately $1.00 per 1,000 gallons of water treated. This figure is based on use of the solutions only once for regeneration of a casein-formaldehyde-ferric chloride compound. It is likely, however, that the solutions could be re-used. In regeneration of a casein-formaldehyde-hydrochloric acid compound, the cost of regeneration solutions should be about one-third lower than the aforementioned figure, or about 67 cents per 1,000 gallons. Again, this figure does not take into account the possible re-use of the regeneration solutions.

Most of the bed-type and coagulation treatments that have shown promise (by virtue of lowering the COD of Mt. Holly secondary effluent) impart HCl or H_2SO_4 to the effluent. Ionac A-260 resin should offer a solution to this problem. This resin is prone to organic fouling, so it might be necessary for the residual organic contaminants (COD-imparting refractories) to be removed before the treated effluent is passed through Ionac A-260.

It is quite conceivable, even likely, that the organic refractory contaminants removed by these coagulation bed treatments are of the larger molecular species. The larger species are believed responsible for most organic fouling of ion exchange resins. Once removed by the coagulation or bed treatment, the

remaining organic contaminants may not foul the Ionac A-260 resin. A precoagulation might, for the same reason, also permit use of Ionac A-300 or Ionac A-540 resins without organic fouling.

The cost of deacidifying an organic-free effluent, or a non-resin-fouling effluent (containing 200 ppm HCl) with Ionac A-260 is approximately $0.05 per 1,000 gallons. If organic materials are present they must not, of course, compete with the acid for exchange sites. This figure is based on an effluent containing 200 ppm HCl because most of the treatments considered in this study would produce an effluent containing from 150 to 250 ppm acid as HCl. This cost figure includes the resin plus soda ash for regenerating it, but does not include other overhead costs. Ionac A-260 resin costs $50.00 per cubic foot, as does Ionac A-300 resin. Ionac A-540 resin costs $58.00 per cubic foot. These prices are for lots of 400 cubic feet or more. No price data are available for Ionac XLA-400, since it is not currently in production, but it is expected that the cost of this resin will be from $50.00 to $58.00 per cubic foot.

DISCUSSION AND CONCLUSIONS

Adsorbents

No cheap, commercially available solid (such as a mineral or a manufacturer's by-product or scrap) is likely to remove all refractory contaminants found in secondary effluents, at least not as economically as does activated carbon. These solids can, however, be expected to make contributions to advanced waste treatment through removal of specific contaminants.

When employed in the sludge blanket apparatus, finely divided solid adsorbents such as clays and other minerals should have a mesh size of approximately 325. These particles would be fine enough to expose a large surface area yet large enough that they would not be carried over into the clarified zone of treated effluent. If applied in the presence of the floc from a coagulation, however, a much finer particle size can be utilized.

Particle shape of solid materials appears to play only a minor role in adsorption affinity. The major factor is exposed surface area. Hydrous zirconia floc, for example, has many times the adsorptive capacity of dry, ground zirconium oxide.

Coagulants

Coagulation agents fed as liquids or in solution hold more promise than do solid adsorbents in advanced waste treatment. Batch coagulations are not practical for waste treatment, such as tertiary waste treatment, but continuous coagulation procedures such as the sludge blanket process should make substantial contributions to this field.

Lime, ferric chloride, and ferric sulfate, in conventional use now, should continue to contribute to waste treatment technology. These materials contribute inorganic anions to the treated effluents, and these must be disposed lest they, too, build up in objectionable concentrations with re-use of the water.

Coagulation in the presence of most adsorption and ion exchange materials is technically feasible in the sludge blanket process for water treatment. Combining the specific properties of solid adsorbents and ion exchangers with those of coagulants might result in single tertiary treatments for the removal of residual or refractory contaminants from various secondary effluents. Separating the components employed in such mixtures could be accomplished by differences in their settling characteristics. Regeneration of the components by the burning off of adsorbed contaminants, or by other techniques, could then be accomplished. This process could be as cheap as, or cheaper than, treatments involving activated carbon.

The natural supply of minerals and other inorganic materials should not be considered to be endless. The known occurrence of many minerals is confined to only limited geographical areas. From this standpoint, treatments involving organic products, such as carbons and proteins (which can be produced in a theoretically unending supply and in most geographic areas) would appear to hold an edge on mineral treatments. Suitable regeneration techniques and cost factors in regeneration could, however, reverse this thinking.

Costs

The cost of tertiary treatments is difficult to define. Seasonal, even daily, variations occur in the number of contributing refractory species and in the proportions of these materials, one to the other. These variations can affect the cost of tertiary treatments. The writers have noted that the higher the COD of prefiltered Mt. Holly secondary effluent, the greater is the drop in COD as a result of a given treatment.

RECOMMENDATIONS

As a result of our efforts and findings during this study, we make the following recommendations concerning analytical procedures:

(a) Specific tests should be developed to analyze and correct for the presence of residual treatment agents in treated effluents where these residual agents interfere with the tests used to measure quality improvement due to a treatment. Such analyses would also be valuable for prescribing maximum treatment dosages.

(b) More thought should be given to the standard pretreatment (filtration through Whatman No. 5 paper) and preanalyses of effluent prior to testing and posttreatment analysis with a view toward improving the reliability of the results of treatments involving different effluent samples obtained from the same source.

(c) Techniques of infrared and ultraviolet analysis should be included to obtain indices for the measurement of refractory contaminant concentration in waste-water samples before and after treatment.

The writers further recommend that the following projects be included in the Advanced Waste Treatment Program of the United States Public Health Service:

(a) Studies of coagulation techniques employing filtered versus unfiltered effluents to ascertain whether the presence of the particulate matter will enhance adsorption of refractory contaminants and, if so, to take advantage of these properties;

(b) study of quaternization of both hydrophilic and hydrophobic proteins to increase (cheaply) their affinity for organic refractory contaminants in waste waters;

(c) study of cross-linking of both hydrophilic and hydrophobic proteins to stabilize them cheaply for use in removal of refractory contaminants from waste waters;

(d) comprehensive study of the effects of selected solid adsorbents, as treated with selected chemical treatment solutions (such as salts of tetravalent metals, and mineral acids) on the refractory contaminants in secondary effluents;

(e) study of the feasibility of employing electrolytic technology [illegible] regeneration of adsorbents;

(f) study of the acceleration of regeneration of solid adsorbents by ultrasonic excitation techniques, [10] with

emphasis on anionic refractory contaminants as adsorbed from waste effluents;

(g) study of regeneration of adsorbents and ion exchangers by the enzymatic action of bacteria and molds;

(h) study of the feasibility of selective breeding of bacterial and mold strains for degradation of troublesome organic materials.

REFERENCES

1. Bunch, R. L., Barth, E. F., and Ettinger, M. B., Organic Content of Secondary Sewage Effluents, U.S. Dept. of Health, Education, and Welfare, Robert A. Taft Sanitary Engr. Center, Cincinnati, Ohio.
2. Mueller, H. F., et al., Chromatographic Identification and Determination of Organic Acids in Water, Anal. Chem., 30:41, 1958.
3. Painter and Bywater, J. Inst. Sew. Purif. p. 302, 1960.
4. Carpenter, C., and Porter, C., Waste Water Utilization by Clarification, TAPPI Annual Meeting, New York, N. Y., Feb. 1945.
5. Kirk, R. E., and Othmer, D. F., (Editors), Encyclopedia of Chemical Technology, 8:63.
6. U.S. Patent No. 2,393,269: Coagulation Composition for Removal of Suspended or Dissolved Material From Liquids.
7. Anderson, J., Colloid Chemistry, 6:1, 131.
8. U.S. Patent No. 2,758,084: Water Purification Process.
9. Morris, J. C., and Weber, W. J., Jr., Removal of Biochemically Resistant Compounds by Adsorption, U.S. Dept. of Health, Education, and Welfare, Public Health Service Publication No. 999-WP-11, AWTR-9.
10. Ultrasonic Leaching of Simulated Calcined Wastes, U.S. Atom. Energ. Comm., NYO-2577, 1960. Wat. Pollut. Abstr., (#1726), 34, (#9) 319, Sept. 1961. Nuclear Sci. Abstr., 15, 754, 1961.

GPO 812-253-6

SELECTED READINGS

1. Morgan, J.J., and Engelbrecht, R.S., Effects of Phosphates on Coagulation and Sedimentation of Turbid Waters, J. Amer. Wat. Wks, Assoc. (JAWWA),52, 1303-1314, 1960, Wat. Pollut. Abstr.(WPA)1972, 34, 364, Nov. 1961.

2. Griffin, A.E., Significance and Removal of Manganese in Water Supplies, JAWWA, 52, 1326-1334, 1960, WPA 1982, 34, 365-366, No. 1961.

3. Shatto, H., Aerobic Digestion Plus Diatomite Filter, Publ. Wks. N.Y., 91, 82-83, 1960. WPA 2120, 34, 388-389, No. 1961.

4. CMC Kayoed Stream Pollution, Text. Ind., 124, 161-162, 1960. WPA 2120, 34, 388-389, Nov. 1961.

5. Fitzgerald, G.P., Loss of Algicidal Chemicals in Swimming Pools, Appl. Microbiol., Baltimore, 8, 269-274, 1960. WPA 2144, 34, 392-393, Nov. 1961.

6. Sontheimer, H., Processes of Coagulation and Sedimentation (Paper presented at a water treatment conference in Essen, February 19 0), WPA 1574, 34, 291, Sept. 1961.

7. Maier, F.J., Partial Defluoridation of Water, Publ. Wks., N.Y., 91, 90-92, 1960. WPA 1581, 34, 292, Sept. 1961.

8. Gorodisheher, A.Y., and Mashneva, N.I., De-Activation of Drinking Water Containing Radioactive Phosphorus by the Method of Contact Coagulation, Hyg. and Sanit., Moscow, 25, 56-60, 1960. WPA 1582, 34, 292, Sept. 1961. Nuclear Sci. Abstr. (NSA), 15, 811, 1961.

9. Wedekind, B., Treatment of Waste Waters in the Metal Industry, Metall, 12, 515-519, 1958. WPA 1710, 34, 316, Sept. 1961.

10. Tadsen, V.S., Lime Neutralization of Metal-Bearing Acid Wastes (Paper presented at the 7th Industrial Waste Conf., Ontario, 1960), WPA 1711, 34, 316, Sept. 1961.

11. Truelle, M.A., Experiences with Waste Waters from Large-Scale Pig Breeding, Za Socialist Zemed, 7, 943-946, 1957. WPA 1720, 34, 318, Sept. 1961.

12. Thomas, K.T., Jacobs, D.G., Tamura, T., and Struxness, E.G., Strontium Sorption Studies Using Naturally Occurring Ion-Exchange Materials, USAEC, CF-60-10-35, 1960. WPA 1725, 34, 319, Sept. 1961. NSA, 15, 915-916, 1961.

13. Herrmann, W., and Czerwenka, W., Treatment and Improvement of Rhine Water in Krefeld, Gas-U. Wasserfach, 101, 343-345, 1960. WPA 1371, 34, 256, Aug. 1961.

14. Painter, R.A., Hudson, H.S., and Corwin, S., Chesterfield County, Va., Filtration Plant, Wat. and Sewage Wks., 107, 365, 1960. WPA 1373, 34, 256, Aug. 1961.

15. Abasayev, E.S., Preparation and Use of a Ferrous Sulphate Solution as a Coagulant for Preliminary Treatment of Water at the Water Works of Novosibirsk, Vodosn. i Sanit. Tekh., 8-9, 1959. WPA 1378, 34, 257, Aug. 1961.

16. Monferdini, J.A., Activated Silica as a Coagulant Aid, Sthwest. Wat. Wks. J., 42, 20-22, 1960. WPA 1379, 34, 257-258, Aug. 1961.

17. Oeming, L.F., How to Treat Organic-Type Wastes from Industry, Munic. Util., 98, 24-26; 57-60, 1960. WPA 1500, 34, 279, Aug. 1961.

18. Okunj, S.S., The Use of Slag Heaps for the Preliminary Treatment of Some Industrial Waste Waters, Vodosn. i Sanit. Tekh., 13-16, 1959. WPA 1504, 34, 279-280, Aug. 1961.

19. Jacobs, D.G., and Cowser, K.E., Soil Column Studies, USAEC, ORNL-2994, 78-95, 1960. WPA 1520, 34, 282, Aug. 1961. NSA, 15, 149-150, 1961.

20. Cerrai, E., Scaroni, A., and Triulzi, C., The Treatment of Liquid Radioactive Wastes in the C.I.S.E. Radiochemistry Laboratory, Energ. Nucl., Milan, 7, 630-637, 1960. WPA 1518, 34, 282, Aug. 1961. NSA, 15, 150, 1961.

21. Tamura, T., and Jacobs, D.G., Sorption and Retention by Minerals and Compounds, USAEC, ORNL-2994, 58-78, 1960. WPA 1521, 34, 282, Aug. 1961. NSA, 15, 149, 1961.

22. Osherelyava, M.N., Treatment of Waste Waters from the Wool Industry Vodosn. i Sanit. Tekh., 12, 14-15, 1959. WPA 1526, 34, 283, Aug. 1961.

23. Jankovic, S.D., and Milojevic, M.B., Transformation of Coal Ashes into Mixed Coagulants for Water Treatment, Bull. Centre belge Et. Document. Eaux, 47, 50-53, 1960. WPA , 34, 191, June 1961.

24. Malaney, G.W., Oxidative Abilities of Aniline-Acclimated Activated Sludge, J. Wat. Pollut. Contr. Fed. (JWPCF), 32, 1300-1311, 1960. WPA 1106, 34, 208, June 1961.

25. Humphreys, F.C., Sewage Effluent in Use as Power Plant Circulating Water, Proc. 14th Industr. Waste Conf., Purdue Univ. Engng. Extn. Ser., No. 104, 732-742, 1959. WPA 877, 34, 165, May 1961.

26. Solin, V., The Purification of Generator Effluents by Means of Slag Filters. Results Obtained by the Sanitation Works at Dubnika, Sci. Pap. Inst. Chem. Technol., Prague, Fac. Technol. Fuel Wat., 3, Pt. 1, 149-175, 1959. WPA 909, 34, 171, May 1961.

27. Gilliam, A.S., and Anderegg, F.C., Biological Disposal of Refinery Wastes, Proc. 14th Industr. Waste Conf., Purdue Univ. Engng. Extn. Ser., No. 104, 145-154, 1959. WPA 915, 34, 172, May 1961.

28. Madarasz, M.F., Pilot-Plant Recovery of an Iron Coagulant from Oil Waste Treatment Sludge, Proc. 14th Industr. Waste Conf., Purdue Univ. Engng. Extn. Ser., No. 104, 191-199, 1959. WPA 916, 34, 172, May 1961.

29. Norton, P.A.L., Radioactive Effluents, Chem. Tr. J., 147, 987-988, 1960. WPA 919, 34, 173, May 1961.

30. Ames, L.L., Zeolitic Extraction of Caesium from Aqueous Solutions, USAEC, H.W.-62607, 1959. WPA 920, 34, 173, May 1961. NSA, 14, 2578, 1960.

31. Rhodes, D.W., Adsorption by Soil of Strontium from 216-S Crib Waste, USAEC, H.W.-42699. WPA 923, 34, 174, May 1961. NSA, 14, 2254, 1960.

32. A Review of the Literature of 1959 on Waste Water and Water Pollution Control-U.S. Water Pollution Control Federation, JWPCF, 32, 443-481, 545-593, and 681-720, 1960. WPA 2244, 33, 417, Dec. 1960.

33. Blakeley, C.P., Old and New Procedures in Water Coagulation, Publ. Wks., N.Y., 90, No. 12, 111-115, 164, and 166-167, 1959. WPA 1963, 33, 364, Nov. 1960.

34. Christ, W., and Scholg, L., The Use of Activated Silica as a Coagulant Aid in Water Treatment, Wasserw.-Wass Techn., 8, 361, 1958. WPA 1736, 33, 327, Oct. 1960.

35. MacGonagle, F.R., Silica Sols in Water Treatment, Wat. and Sewage Wks., 106, 541-543, 1959. WPA 1737, 33, 327, Oct. 1960.

36. Tuepker, J.L., and Hartung, H.O., Effect of Accumulated Lime-Softening Slurry on Magnesium Reduction, JAWWA, 52, 106-116, 1960. WPA 1742, 33, 328, Oct. 1960.

37. Ioanid, G., Mastacan, G., Bunus, F., Popesco, M., Stanciu, S., and Ciocanel, A., An Investigation on the Use of Roumanian Clays as Ion Exchangers in the Decontamination of Radioactive Wastes, Proc. 2nd U.N. Int. Conf. Peaceful Use Atom. Energ., 18, 598-604, 1958. WPA 1893, 33, 351, Oct. 1960.

38. Bernaud, C., Industrial Problems in the Processing of Radioactive Effluent. Some Specific Solutions Applied at Marcoule, Proc. 2nd U.N. Int. Conf. Peaceful Uses Atom. Energ., 18, 86-89, 1958. WPA 1897, 33, 352, Oct. 1960.

39. Cowser, K.E., Morton, R.J., and Witkowski, E.J., The Treatment of Large-Volume, Low-Level Waste by the Lime-Soda-Softening Process. Proc. 2nd U.N. Int. Conf. Peaceful Uses Atom. Energ., 18, 161-173, 1958. WPA 1900, 33, 353, Oct. 1960.

40. Trom, S., Casselton's New Water-Treatment Plant, Off. Bull. N. Dak. Wat. Wks. Conf., 27, No. 4 & 5, 2, 1959. WPA 1536, 33, 291, Sept. 1960.

41. Misniakievicz, W., The Problem of the Use of Chlorine Dioxide in the Treatment of Water Supplies and Waste Waters, Chemik, 9, 179-180, 1956. Chem. Zbl., 129, 8157, 1958. WPA 1542, 33, 292, Sept. 1960.

42. Filter Plant Removes A-Bomb Fallout in River, Chem. Engng., 67, 60, 1960. WPA 1560, 33, 294, Sept. 1960.

43. Weaver, P.J., Review of Detergent Research Program, JWPCF (Sewage Industr. Wastes), 32, 288-296, 1960.

44. Borshivoi, D., Treatment of Phenolic Waters on Slag, Hyg. and Sanit., Moscow, 22, 54-56, 1957. Chem. Zbl., 129, 7862, 1958. WPA 1660, 33, 313, Sept. 1960.

45. Giebler, G., Studies on the Treatment of Waste Waters of the Pest Control Industry, Vom Wasser, 25, 197-208, 1958. WPA 1667, 33, 314, Sept. 1960.

46. Lesenyei, J., Removal of the Harmful Effect of Radioactive Waste Waters, Hidrol. Kozl., 37, 57-59, 1957. WPA 1672, 33, 315, Sept. 1960.

47. Dieterich, B., Radioactive Matter in Waste and Waste Water, Vom Wasser, 25, 163-180, 1958. WPA 1713, 33, 324, Sept. 1960.

48. Black, A.P., Current Research on Coagulation, JAWWA, 51, 1545-1550, 1959. WPA 1342, 33, 256, Aug. 1960.

49. Mackrle, S., Mackrle, V., and Mican, V., New Knowledge on Filtration in Water Supply Technique, Wasserw.-Wasstechn., 8, 357-360, 1958. LitBer. Wass. Abwass. Luft. U. Boden, 8, 19-20, 1959. WPA 1343, 33, 256, Aug. 1960.

50. Stones, T., The Fate of Nickel During the Treatment of Sewage, J. Inst. Sew. Purif., Pt. 2, 252-254, 1959. WPA 1416, 33, 268, Aug. 1960.

51. Stones, T., The Fate of Zinc During the Treatment of Sewage, J. Inst. Sew. Purif., Pt. 2, 254-257, 1959. WPA 1417, 33, 268, Aug. 1960.

52. Pettit, C.G., 20 Years of Sewage Sludge Burning at Barberton, Ohio, Proc. Amer. Soc. Civ. Engrs. (Pap. No. 2247), 85, SA 6, 17-24, 1959. WPA 1425, 33, 270, Aug. 1960.

53. Fiedler, H., Chemistry, Action, and Range of Application of Synthetic Organic Coagulation and Peptization Agents, Wasserw.-Wasstechn., 8, 561-564, 1958. LitBer. Wass. Abwass. Luft U. Boden, 8, 56, 1959. WPA 1462, 33, 278, Aug. 1960.

54. Hillmeyer, K., Experiments on Removal of Sludge from Brown Coal Suspensions by Flocculation, Braunkohle, Warme U. Enegie, 19/20, 434-435, 1958. Lit Ber. Wass. Abwass. Luft U. Boden, 8, 58, 1959. WPA 1483, 33, 281, Aug. 1960.

55. Knie, K., Cyanide in Water and Waste Water, Wass. U. Abwass., 2, 117-129, 1957. WPA 1486, 33, 282, 1960.

56. Lieberman, J.A., Handling, Treatment, and Disposal of Radioactive Wastes, Aust. Atom. Energ. Symp., 435-446, 1958. NSA, 14, 168-169, 1960. WPA 1492, 33, 283, Aug. 1960.

57. Hofer, P., De-acidification of Acid Waters by Magnesium Oxide and Hydroxide, Gesundheitsing, 80, 15-20, 1959. WPA 1162, 33, 221, July 1960.

58. Stammer, H.A., The Influence of the Media in Percolating Filters on the Treatment of Domestic Sewage, Munch. Beitr. Abwass.-Fisch.-U. Flussbiologie, 5, 32-42, 1958. LitBer. Wass. Abwass. Luft U. Boden, 7, 279, 1958. WPA 1214, 33, 231, July 1960.

59. Gehm, H.W., New Approaches to Pulp and Paper Mill Waste Treatment, Industr. Wastes, 4, 200-204, 1959. WPA 1232, 33, 233, July 1960.

60. Reid, E.F., and Waddington, A.H., The Choice of a Clarifier in the Treatment of Effluents, Proc. Brit. Pap. Bd. Mkrs. Assoc., 39, 391-416, and 441-444, 1958. Bull. Inst. Pap. Chem., 29, 1530, 1959. WPA 1234, 33, 233-234, July 1960.

61. Trembley, J.A., Mihunski, J.A., and Hertz, E.W., Use of Cement Plant Stack Dust as a Neutralizing Agent in Acid Water Lakes, Trans. Northeast Wildl. Conf., 1958, 1, 55-60, 1959.

62. Solin, V., and Erlebach, J., Treatment of Mono- and Di-valent Phenols on Boiler Slag, Voda, 36, 276-278, 1957. Chem. Zbl., 129, 5478, 1958. WPA 1243, 33, 235, July 1960.

63. Sedlander, N. R., Effect of Alkylbenzene Sulphonate on Characteristics of Hydrous Alumina Floc, Diss. Abstr., 19, 3272, 1959. J. Appl. Chem., London, 9, ii-533, 1959. WPA 980, 33, 186, June 1960.

64. Genge, J. A. R., Ion Exchange (Inorganic Technological Applications), Chem. Process Engng., 40, 352-354, 1959. WPA 984, 33, 186, June 1960.

65. Willems, J., Formation of Complexes with Calcium, Parfum. U. Kosmet, 37, 38, 590-594 & 655-668, 9-16, and 72-82, 1956, 1957. WPA 986, 33, 187, June 1960.

66. Woodward, R. L., and Robeck, G. G., Removal of Radiological, Biological, and Chemical Contaminants from Water, Robert A. Taft Sanitary Engineering (RATSEC) Center Tech. Rep. W59-2, 1959. Public Health Engng. Abstr. (PHEA), 39, 37 (W:39), 1959. WPA 992, 33, 188, June 1960.

67. Kaess, A., Materials in Industrial Wastes Which Pass Primary Clarifiers, and Means of Removing Them, XVII Int. Congr. Chem., 2, 92-93, 1959. J. Appl. Chem., London, 9, ii-532, 1959. WPA 1091, 33, 208, June 1960.

68. Maekawa, Y., Water Softener from Coal, Netsu-Kanri, 8, 22-25, 1956. Chem. Abstr. (CA), 53, 19233, 1959. WPA 774, 33, 149, May 1960.

69. Miller, E. F., Iron and Manganese Removal from Municipal and Industrial Water Supplies, Wat. and Sewage Wks., 106, R. 252-R. 260, 1959. WPA 779, 33, 150, May 1960.

70. Hanning, H., Removal of Organic Substances from Impure Water by Filtration from a Suspension, Mitt. Ver. Grosskesselbesitz, No. 60, 179-181, 1959. CA, 53, 19233, 1959. WPA 780, 33, 150, May 1960.

71. Hubele, Some Experiences with Treatment Methods for Industrial Waste Waters, Ber. Abwass. Tech. Verein, No. 8, 274-290, 1957. WPA 895, 33, 169-170, May 1960.

72. Jung, H., Treatment of Waste Waters from Oil Refineries, Ber. Abwass. Techn. Verein, No. 8, 100-109, 1957. WPA 919, 33, 174-175, May 1960.

73. Bezuglyi, D. V., Purification of Industrial Waste Water by the Method of Retarded Precipitation, Zh. Prikl. Khim, Leningr., 32, 1624-1626, 1959. CA, 53, 20638, 1959. WPA 926, 33, 176, May 1960.

74. Spitsyn, V. I., Concentration, Purification, and Storage of Radioactive Wastes, Prakt. Chem., 10, 86, 88, 91-96, and 98, 1959. J. Appl. Chem., London, 9, ii-314-315, 1959. WPA 934, 33, 178, May 1960.

75. West, G., Iron and Manganese Removal at Lake Charles, La., Wat. and Sewage Wks., 106, 398-399, 1959. WPA 585, 33, 111, April 1960.

76. Sammons, L. L., Removal of Hydrogen Sulphide from a Ground Water Supply, JAWWA, 51, 1275-1276, 1959. WPA 586, 33, 111, April 1960.

77. Cohen, J. M., Rourke, G. A. and Woodward, R. L., Ferric Sulphate Coagulation in the Presence of Synthetic Detergents, JAWWA, 51, 1255-1267, 1959. WPA 588, 33, 111-112, April 1960.

78. Eichholz, G.G., and Roberts, W.N., The Adsorption of (Radioactive) Tracers on Mineral Particles, 2nd U.N. Int. Conf. Peaceful Uses Atom. Energ. A/Conf. 15/P/217, 1958. WPA 679, 33, 129, April 1960.

79. Flynn, J.L., Crash Program for Expensive Water, Proc. 13th Industr. Waste Conf., Purdue Univ. Engng. Extn. Ser., No. 96, 253-259, 1958. WPA 698, 33, 133, April 1960.

80. Burns, R.H., and Glueckauf, E., Developement of a Self-Contained Scheme for Low Activity Wastes, 2nd U.N. Int. Conf. Peaceful Uses Atom. Energ. A/Conf. 15/P/308, 1958. WPA 714, 33, 136, April 1960.

81. Dejonghe, P., Treatment of Radioactive Effluents at the Mol Laboratories, 2nd U.N. Int. Conf. Peaceful Uses Atom. Energ. A/Conf. 15/P/1676, 1958. WPA 715, 33, 136-137, April 1960.

82. Vosnesensky, S.A., Serada, G.A., Dolgikh, P.F., and Baskov, L.I., Decontamination of Low-Saline and Low-Active Effluents of Radiochemical Industries, 2nd U.N. Int. Conf. Peaceful Uses Atom. Energ. A/Conf. 15/P/2024, 1958. WPA 718, 33, 137-138, April 1960.

83. Ames, L.L., McHenry, J.R., and Honstead, J.F., The Removal of Strontium from Wastes by a Calcite-Phosphate Mechanism, 2nd U.N. Int. Conf. Peaceful Uses Atom. Energ. A/Conf. 15/P/395, 1958. WPA 724, 33, 139, April 1960.

84. Milione, M., Cetini, G., and Ricca, F., The Elimination of Radioactive Elements from Aqueous Solutions; Cetini, G., and Ricca, F., The Use of Basic Silica Gel for the Elimination of Radio-elements from Aqueous Solutions, (Abstracts) 2nd U.N. Int. Conf. Peaceful Uses Atom. Energ. A/Conf. 15/P/1515, 1958. WPA 725, 33, 139, April 1960.

85. Klechkovsky, V.M., Tselischeva, G.N., and Sokolova, L.N., Sorption of Tracer Amounts of Strontium and Cesium in Soils, 2nd U.N. Int. Conf. Peaceful Uses Atom. Energ. A/Conf. 15/P/2310, 1958. WPA 726, 33, 139, April 1960.

86. Reichelt, H., Magnesium and Sodium Ions in the Decarbonization of Water, Brauwelt, B.96, 1169-1172, 1956. Chem. Zbl., 129, 2295, 1958. WPA 439, 33, 80-81, March 1960.

87. Lacy, W.J., Rollins, R.R., and Lawless, L.M., The Removal of Radioactive Material from Water by Serial Coagulation, by Ion Exchange, and by Charcoal Adsorption, USAEC, ERDL-1451-RR., 1956. NSA, 13, 2104-2105, 1959. WPA 444, 33, 81-82, March 1960.

88. Meerman, P.G., The Sedimentation of Coal Industry Waste Waters, Bull. Centre Belge Et. Document. Eaux, No. 45, 150-153, 1959. WPA 545, 33, 103, March 1960.

89. Lutter, E., Removal of Toxicity from and Neutralization of Waste Waters, Metallwarenind, No. 7, 280, 1958. Gas U. Wasserfach, 99, 1183-1184, 1958. WPA 550, 33, 104, March 1960.

90. Smit, J.V.R., Robb, W., and Jacobs, J.J., A.M.P.-Effective Ion Exchanger for Treating Fission Wastes, Nucleonics, 17, 9, 116, 118, and 120-123, 1959. WPA 563, 33, 106, March 1960.

91. Report on Research Carried Out by the Public Health Engineering Section, 1948-1955, Dept. Civ. Engng., Kings' Coll., Newcastle, Bull. No. 6, 1956. WPA 222, 33, 40, Feb. 1960.

92. Report on Research Carried Out by the Public Health Engineering Section in the Year Ended 30th June, 1956, Dept. Civ. Engng. Kings' Coll., Newcastle, Bull. No. 9, 1957. WPA 223, 33, 40, Feb. 1960.

93. Zubcenko, D., Activated Silica as an Aid to Coagulation, Voda, 132-134, 1957. Chem. Zbl., 129, 1111, 1958. WPA 225, 33, 41, Feb. 1960.

94. Woxholt, W.G., Electrical Conductivity and the Stability of Colloids, JAWWA, 51, 885-889, 1959. WPA 227, 33, 41, Feb. 1960.

95. Scherer, C.H., and Alexander, D.E., Waste Water Transformation at Amarillo, I. Municipal Phase. II. Industrial Phase. Sewage Industr. Wastes (SIW), 31, 1103-1108, 1959. WPA 330, 33, 59-60, Feb. 1960.

96. Reploh, H., and Kustermann, H., Investigations on the Delay in Flocculation of Iron Hydroxide in Waste Waters Caused by Organic Matter, Gas-U. Wasserfach, 99, 1066-1068, 1958. WPA 333, 33, 60, Feb. 1960.

97. Palin, A.T., Controlled Filter Breakthrough by the Addition of Activated Silica to Settled Water, Wat. and Wat. Engng., 63, 258-259, 1959. WPA 6, 33, 1, Jan. 1960.

98. Klinge, L.N., Tels, M., Waale, M.J., and Waterman, H.I., Fatty Oils to Remove Taste and Odor, Wat. & Sewage Wks., 106, 237-238, 1959. WPA 42, 33, 7, Jan. 1960.

99. McGill, J.F., and Hulla, G., Hydrogen Sulphide and Iron Occurrence and Removal from Domestic Water, Sanitarian, Los Angeles, 21, 29-32, July-August, 1958. PHEA, 39, 35-36 (W:19-W:20), 1959. WPA 43, 33, 7, Jan. 1960.

100. Nikolaev, A.V., Samusenko, A.P., and Tush, K.N., Removal of Silica from Industrial Waters by Aid of Magnesia-Containing Sorbents, Pwr. Sta., Moscow, 29, 26-28, 1958. CA, 53, 13460, 1959. WPA 48, 33, 8, Jan. 1960.

101. Rippert, I., Possibilities of Elimination of Phosphate from Sewage by Chemical Methods, Gesundheitsing, 79, 333-337, 1957. WPA 128, 33, 22, Jan. 1960.

102. Sarkisyan, M.A., and Zakharyan, R.A., Extraction of the Trivalent Chromium from Tannery Wastes by Using Armenian Clays, Bull. Acad. Sci. Armyan, S.S.R., Tech. Sci. Ser., 12, 59-62, 1959. CA, 53, 13462, 1959. WPA 168, 33, 29, Jan. 1960.

103. Girand, J., Production of Bicarbonate Alkalinity, JAWWA, 51, 728-732, 1959. WPA 2156, 32, 398, Dec. 1959.

104. Renn, C.E., and Barada, M.F., Adsorption of ABS on Particulate Materials in Water, SIW, 31, 850-854, 1959. WPA 2178, 32, 401, Dec. 1959.

105. Beneden, G.V., Study on the Removal of Mineral Iron and Humic Materials from Water, Bull. Centre Belge Et. Document Eaux, 43, 49-53, 1959. WPA 2180, 401-402, Dec. 1959.

106. Zamorani, E., and Pizziolo, A., The Removal of Radiostrontium from Water, 5th Int. Electron. & Nuclear Rev., Acta Scie. Congr., 1, 233-247. NSA, 13, 1281, 1959. WPA 2183, 32, 402, Dec. 1959.

107. Kulskii, L.A., Koganovsii, A.M., Machorin, K. J., Kalinitschuk, J.M., Tschertov, W.M., and Dikolenko, J.I., Production of Activated Anthracite Suitable for Treatment of Waste Waters from the Aniline Dye Industry, J. Chim. Ukr., 23, 117-121, 1957. Chem. Zbl., 128, 13454-13455, 1957. WPA 2296, 32, 423, Dec. 1959.

108. A Review of the Literature of 1958 on Sewage, Waste Treatment, and Water Pollution. (U.S. Federation of Sewage and Industrial Wastes Associations), SIW, 31, 501-541, 615-661, and 763-803, 1959. WPA 2252, 32, 414, Dec. 1959.

109. Metzler, D.F., The Re-Use of Treated Waste Water for Domestic Purposes, Publ. Wks., N.Y., 90, No. 5, 117-119 & 208, 209, 1959. WPA 1967, 32, 366, Nov. 1959.

110. Kulskii, L.A., Shevchenko, M.A., and Lempke, G.J., Prospects in the Use of Activated Silica in the Treatment of River Water, Vodosn. Sanit. Tekh., No. 11, 24-27, 1956. Chem. Zbl., 128, 11978, 1957. WPA 1976, 32, 367, Nov. 1959.

111. Boelhouwer, C., Syderius, R., Tels, M., and Waterman, H.I., Fatty Oils for Odor Removal, Wat. and Sewage Wks., 106, 188-190, 1959. WPA 1986, 32, 368, Nov. 1959.

112. Markaryants, M.K., and Shtannikov, E.V., The Problem of Radioactivity and Water Supply and Sanitary Protection of Water Sources, Tekh. Dokl. XIII Sedza Gig., Epid. Mikrobiol. Infekt., Moscow, 1, 55-57, 1956. PHEA, 39, 22 (PHP:2), 1959. WPA 1991, 32, 369-370, Nov. 1959.

113. Scholl, O., Sewage Treatment, Dtsch. Molkztg., 78, 4-5, 1957. Chem. Zbl., 128, 11979, 1957. WPA 2067, 32, 381, Nov. 1959.

114. McKinney, R.E., and Donovan, E.J., Bacterial Degradation of ABS II. Complete-Mixing Activated Sludge, SIW, 31, 690-696, 1959. WPA 2071, 32, 382, Nov. 1959.

115. McKinney, R.E., and Symons, J.M., Bacterial Degradation of ABS I. Fundamental Biochemistry, SIW, 31, 549-556, 1959. WPA 1864, 32, 345, Oct. 1959.

116. Pettet, A.E.J., Tomlinson, T.G., and Hemens, J., Treatment of Strong Organic Wastes by Anaerobic Digestion, Surveyor, Lond., 118, 481-482, 1959. WPA 2105, 32, 388, Nov. 1959.

117. Bernhardt, H.F., Toxic Wastes made Harmless-Automatically, Instrumentation, 11, 20-21, July-August, 1958. WPA 2120, 32, 391, Nov. 1959.

118. Iwai, S., Aida, K., and Inoue, Y., Processing of Radioactive Waste by Ion-Exchange Method, Dai-I-Kai Genskiryoku Symposium Hobushu, 571-574, 1957. CA, 53, 11724, 1959. WPA 2128, 32, 393, Nov. 1959.

119. Wright, T.D., and Monohan, J., Optimum Conditions for the Use of Vermiculite in the Decontamination of Radioactive Effluent, U.K. Atom. Energ. Author., AERE-ER-2707, 1958. NSA, 13, 439, 1959. WPA 1726, 32, 321, Sept. 1959.

120. Fong, W., Non-Ionic Detergents in Raw-Wool Scouring, Including Studies of Waste Clarification, Amer. Dyest. Rep., 48, P45-P50, 1959. CA, 53, 5685, 1959. WPA 1728, 32, 321, Sept. 1959.

121. Connell, C.H., and Berg, E.J.M., Industrial Utilization of Waste Water, SIW, 31, 212-220, 1959. WPA 1486, 32, 277, Aug. 1959.

122. Dickey, C.L., How Polyacrylamide-Type Flocculants Help Solve Mill Problems, Paper Tr. J., 142, No. 31, 34-36, 1958. Bull. Inst. Pap. Che., 29, 582, 1958. WPA 1500, 32, 279, Aug. 1959.

123. Pilipovich, J.B., Black, A.P., Eidsness, F.A., and Stearns, T.W., Electrophoretic Studies of Water Coagulation, JAWWA, 50, 1467-1482, 1958. WPA 1171, 32, 222, July 1959.

124. Brown, J.G., Reversible Diatomite Filtration, Wat. and Sewage Wks., 105, 456-461, 1958. WPA 1177, 32, 223, July 1959.

125. Speeg, D.E., Polyphosphate Treatment, Wat. and Sewage Wks., 105, 538-540, 1958. WPA 1194, 32, 226, July 1959.

126. Masing, L.A., and Busslajeva, N.S., Use of Activated Silicate for Coagulation in Waste Waters, Pap. Industry, Moscow, 31, No. 10, 13-14, 1956. WPA 1290, 32, 241, July 1959.

127. Ongerth, H.J., and Harmon, J.A., Sanitary Engineering Appraisal of Waste Water Re-Use, JAWWA, 51, 647-658, 1959. WPA 2078, 32, 383, Nov. 1959.

128. Scherer, C.H., Sewer Plant Effluent is Cheaper than City Water, Wastes Engng., 30, 124-127, 1959. WPA 2056, 32, 380, Nov. 1959.

129. Proceedings of the Thirty-Ninth Texas Water and Sewage Works Short School, 1957. WPA 1745, 32, 326, Oct. 1959.

130. Logsdail, D.H., Treatment and Disposal of Radioactive Wastes, Industr. Chem., 35, 213-220, 1959. WPA 1917, 32, 355-356, Oct. 1959.

131. Craven, B.R., and Green, J.H., Exchange Capacities of some Sydney Soils for Strontium Ions, Aust. J. Appl. Sci., 10, 104-112, 1959. WPA 1920, 32, 356, Oct. 1959.

132. Dris, I.A., Coagulation of Water by Aluminum Sulphate Following Precipitation with Aluminum Hydroxide, Vodosn. i Sanit. Tekh., No. 12, 10-11, 1958. CA, 53, 7471, 1959.

133. Black, A.P., Ball, A.I., Black, A.L., Boudet, R.A., and Campbell, T.N., Effectiveness of Polyelectrolyte Coagulant Aids in Turbidity Removal, JAWWA, 51, 247-263, 1959. WPA 1576, 32, 293, Sept. 1959.

134. Howe, R.H.L., What to do with (Sewage) Supernatant?, Wastes Engng., 30, 12-15 and 35, 1959. WPA 1681, 32, 314, Sept. 1959.

135. Drabek, B., Treatment of Phenolic Waters by Adsorption on Slag, Gaz., Woda Tech. Sanit., 30, 448-451, 1956. Chem. Zbl., 128, 8318, 1957. WPA 1301, 32, 243, July 1959.

136. Higgins, I.R., and Messing, A.F., Development of a Continuous Ion-Exchange Process for the Removal and Recovery of High-Purity Caesium from Alkaline Waste, ORNL-2491 Office of Technical Services, U.S. Dept. of Commerce, Wash., D.C., 1958. NSA, 13, 68, 1959. WPA 1309, 32, 244, July 1959.

137. Hollis, E.T., and Dixon, H.E., Removal of Molybdenum from Acid Leach Liquors by Activated Carbon, WIN-53 Office of Tech. Services, U.S. Dept. Commerce, Wash., D.C., 1958. NSA, 13, 123, 1959. WPA 1310, 32, 244, July 1959.

138. Waddington, A.H., Pilot Plant for Water Treatment, Proceedings of the Soc. for Wat. Treatment and Examination, 10, Pt. 1, 1961.

139. Water Treatment Handbook (Degremont Acfi), 1960.

140. Klinger, L.L., Improvement in the Coagulation of Surface Waters with Activated Silica, TAPPI, Annual Meeting, 1946.

141. Norens, R.E., The Use of Activated Silica in the Coagulation of Highly Colored Water, TAPPI, Annual Meeting, 1945.

142. Dickinson, B.N., Abrams, I.M., and Benezra, L., Fast Flow Rate Deionization Pressure Drops and Removal of Trace Quantities of Metal Ions, Industrial & Engineering Chem., 51, 1051, Sept. 1959.

143. Farnand, J.R., et al., Spherical Agglomeration of Solids in Liquid Suspension, Canadian Journal of Chem. Engng., 39, 94, April 1961.

144. Training Manual for Course "Organic Chemicals in Water," RATSEC, USDHEW, PHS.

145. Middleton, F.M., and Rosen, A.A., Organic Contaminants Affecting the Quality of Water, Public Health Reports, 71, 1125-113, Nov. 1956.

146. Eitel, W., The Physical Chemistry of the Silicates (University of Chicago Press).

147. Kaufmann, H.P., and Malz, F., Adsorptive Precipitation and Foaming (Skimming) of Detergents from Aqueous Solutions, Fette, Seifen, Anstrichmittel, 62, 1024, 1960.

148. Eckenfelder, W.W., Jr., and Barnhart, E., Removal of Synthetic Detergents from Laudry and Laundromat Wastes (New York State Water Pollution Control Board Research Report No. 5).

149. Halton, J.E., and Graham, J.V., Laundry Water Recovery by Flotation Clarification (U.S. Naval Civil Engng. Laboratory Tech. Report 081).

150. Abrams, I.M., and Lewon, S.M., Removal of Alkyl Benzene Sulfonate from Water by Chloride Cycle Anion Exchange, 138th Meeting of the American Chem. Soc., Sept. 1960.

151. Wilson, A.L., The Removal of Fulvic Acids by Water Treatment Plant, J. Appl. Chem., London, 10, 377-384, 1960. WPA 1773, 34, 328-329, Oct. 1961.

152. Jacobs, D.G., Sorption of Caesium by Conasauga Shale, Health Phys., 4, 157-163, 1960. NSA, 15, 1351, 1961. WPA 1891, 34, 348-349, Oct. 1961.

153. Bensen, D.W., Review of Soil Chemistry Research at Hanford, USAEC, H.W.-67201, 1960. NSA, 15, 1071, 1961. WPA 1892, 34, 349, Oct. 1961.

154. Morgan, J.J., and Engelbrecht, R.S., Effects of Phosphates on Coagulation and Sedimentation of Turbid Waters, JAWWA, 52, 1303-1314, Oct. 1960.

155. Conley, W.R., and Pitman, R.W., Innovations in Water Clarification, JAWWA, 52, 1319-1325, Oct. 1960.

156. Black, A.P., Basic Mechanisms of Coagulation, JAWWA, 52, 492-504, April 1960.

157. Black, A.P., and Christman, R.F., Electrophoretic Studies of Sludge Particles Produced in Lime-Soda Softening, JAWWA, 53, 737-747, June 1961.

158. Black, A.P., and Hannah, S.A., Electrophoretic Studies of Turbidity Removal by Coagulation with Aluminum Sulphate, JAWWA, 53, 438-452, April 1961.

159. Black, A.P., and Williams, D.G., Electrophoretic Studies of Coagulation for Removal of Organic Color, JAWWA, 53, 589-604, May 1961.

160. Foster, R.F., Junkins, R.L., and Linderoth, C.E., Waste Control at the Hanford Plutonium Production Plant, JWPCF, 33, 511-529, May 1961.

161. Middleton, F.M., The Problem of Refractory Substances in Water and Wastes (Paper presented at A.I.C.H.E. Meeting, 12/6/61, New York, N.Y.), RATSEC, USDHEW, PHS.

162. Stephan, D.G., Possible Water Renovation Processes (Paper presented at A.I.C.H.E. Meeting, New York, N.Y., 12/6/61), RATSEC, USDHEW, PHS.

163. Hellman, J.L., Use of Industrial Water Discharged from Sewage Treatment (Paper presented at A.I.C.H.E. Meeting, New York, N.Y., 12/6/61).

164. Hem, J.D., Complexes of Ferrous Iron with Tannic Acid, Geological Survey Water-Supply Paper 1459-D, U.S. Dept. of Int., 1960.

165. Weyermuller, G., Needed: Synthetic Detergents more Easily Removed from Waste Water, Chem. Processing, 25-27, 59, March 1961.

166. Weyermuller, G., Companies Search for Solution to Detergent Wastes, Chem. Processing, 36-39, April 1961.

167. Lieber, M., Syndet Removal from Drinking Water Using Activated Carbon, Wat. & Sewage Wks., 107, 299-301, 1960. WPA 990, 34, 188, June 1961.

168. McGauhey, P.H., and Klein, S.A., Removal of ABS by Sewage Treatment, SIW, 31, 877-899, 1959. WPA 2269, 32, 416, Dec. 1959.

169. Erlebach, J., Stockelova, J., and Solin, V., Contribution to the Problem of Purification of Generator Effluents by Means of Slag Filters. Removing of Fatty Acid by Slag, Sci. Pap. Inst. Chem. Technol., Prague, Fac. Technol. Fuel. Wat., 3, Pt 1, 177-189, 1959. WPA 910, 34, 171, May 1961.

170. B.P. 830,964: Water Purification, WPA 1393, 34, 259-260, Aug. 1961.

171. B.P. 808, 906: A Plant for a Continuous Process for Purification, Treatment, and Utilization of Liquids, in Particular, Waste Water, WPA 1488, 34, 276-277, Aug. 1961.

172. U.S. P. 2,903,424: Treatment of Wool-Scouring Waste, WPA 1527, 34, 283, Aug. 1961.

173. B.P. 812, 228: Clarification of Aqueous Organic Suspensions, WPA 1096, 34, 206, June 1961. J. Appl. Chem., London, 10, ii. 11-ii. 12, 1960.

174. French P. 1,123, 970: Treatment of Water, Chem. Zbl., 129, 9033, 1958. WPA 2172, 33, 401, Dec. 1960.

175. G.P. 967, 190: Softening of Water, Chem. Zbl., 129, 8440, 1958.

176. U.S. P. 2,884,378: Removal of Urochrome from Otherwise Potable Water, CA, 53, 19244, 1959. WPA 781, 33, 150, May 1960.

177. Belgian P. 544, 348: Flocculation Agent for Waste Water Treatment, WPA 674, 33, 128, April 1960.

178. Belgian P. 528, 824: Clarification of Water, CA, 53, 14392, 1959.

179. B.P. 799,621: Method for Clarifying Water, WPA 2158, 32, 398, Dec. 1959.

180. B.P. 769, 121: Improvements in or Relating to a Process of Treating Radioactive Liquids so as to Reduce Their Radioactivity, WPA 2325, 32, 428, Dec. 1959.

181. B.P. 804,638: Improvements Relating to Filtering Apparatus, WPA 1889, 32, 351, Oct. 1959.

182. B.P. 805,526: Clarification of Water, WPA 1577, 32, 294, Sept. 1959. CA, 53, 7475, 1959.

183. U.S.P. 2,866,759: Compositions for Treating Water, CA, 53, 6497, 1959. WPA 1578, 32, 294, Sept. 1959.

184. Japan P. 7,735 (1958): Clarification of Muddy Solutions by Precipitation with Alkylpyridinium Derivatives, CA, 53, 4624-4625, 1959. WPA 1579, 32, 294, Sept. 1959.

185. G.P. (D.D.R.) 9,800: Final Purification of Surface Waters after Flocculation Treatment, CA, 53, 4624, 1959. WPA 1580, 32, 294, Sept. 1959.

186. U.S.P. 2,862,880: Clarification of Water by Use of Hydrophobic Polyamines, CA, 53, 6498, 1959.

187. French P. 1,214,570: Process and Equipment for Rendering Radioactive Wastes Innocuous, NSA, 15, 1351, 1961. WPA 1884, 34, 348, Oct. 1961.

188. U.S.P. 2,948,677: Bioflotation Treatment of Oil-Containing Waste Water.

189. Report on The Recovery of Orthonitrochlorobenzene from the Mississippi River, USDHEW, PHS.

190. * McCallum, G.E., The National Water Quality Program.

191. * Berger, B.B., Objectives of Seminar on Advanced Waste Treatment Research.

192. * Williams, R.T., Analytical Problems.

193. *Skomoroski, R.M., and Eldib, I.A., Foam Fractionation Applied to Removal of Soluble Organic Contaminants from Waste Water Effluents.

194. *Rubin, E., and Everett, Jr., R., Feasibility Study: Foam Separation as a Means of Purification of Activated Sludge Sewage Plant Effluents.

195. *Hickman, K.C., Distillation as an Agent in Sewage Recycle.

196. *Rose, A., and Sweeney, R.F., Water Cleansing by Partial Freezing Processes.

197. *Stern, G.S., Oxidation Project: Advanced Waste Treatment Laboratory.

198. *Sukenik, V.A., and Joyce, R.S., Activated Carbon in Waste Water Treatment-Adsorption and Thermal Reactivation.

199. *Morris, J.C., and Weber, W.J., Adsorption for Removal of Biologically Resistant Materials from Waste Water.

200. *Johnson, R.L., et al., Activated Carbon in Tertiary Waste Treatment-Adsorption and Chemical Reactivation.

201. *Berger, C., and Chew, H.L., The Removal of ABS and Other Refractories from Water By Electrodialysis and Associated Means.

202. *Koenig, L., Ultimate Disposal: Costs and Logistics.

203. *Gregor, H.P., Utilization of Ion-Exchange Membranes Electrodialysis and Ion Exchange Adsorbents in Advanced Waste Treatment.

204. *Gerstler, J.A., Distillation of Waste Waters for Reuse.

205. Richardson, W., and Driscoll, E.D., Demineralizing Experiences at Pennsylvania Power Co. (Paper presented at 22nd Annual Conference of the Engineer's Society of Western Pennsylvania, Pittsburgh, October 1961).

206. Fuchs, W., Humic Acids and Possible Interference in Feed Water Chemistry, Mitt. VGB No. 42, 139-142, 1956.

207. Ungar, J., Naturally Occurring Organic Matter in Water. Polymeric Coagulant Aids (Unpublished).

208. Ungar, J., Naturally Occurring Organic Matter in Water. Protective Colloids (Unpublished).

209. Ungar, J., Mercurimetric Determination of Chlorides Chemistry and Industry, p. 453-454, 1954.

210. Ungar, J., Determination of Ultimate Capacity of Weakly Acidic and Mixed Acid Cation Exchange Resins, Analytical Chemistry, 34, 413, March 1962.

211. Sard, B., and Ungar, J., Determination of Alkalinity and Total Cations in Water, Chemistry and Industry, June, 1955.

212. Pfaudler-Permutit Plans Hot Waste Treater, Chem. & Engng. News, Jan. 9, 46, 47, 1961.

213. Ballinger, D.G., and Lishka, R.J., Reliability and Precision of BOD and COD Determinations, JWPCF, 34, 470-474, May 1962.

---

*Paper presented at Seminar on Advanced Waste Treatment Research, Cincinnati, Ohio, May 1962.

214. Bruce, F.E., Water Pollution Research in Great Britain, Nature, No. 4804, 711, 712.

215. Zapan, M., et al., Preparation of Cation Exchange Material from Sawdust, Celul. Hirtie 6, 278-288, 1957. Chem. Zbl. 130, 6254, 1959. WPA 1576, 34, p. 291, Sept. 1961.

216. Lenchevsky, O., Some Recent Trends in Water Treatment in the U.S.S.R., Eff. and Wat. Treat. Jour., 1, 167-169, Oct. 1961.

217. Boby, W.M.T., Demineralizing Organically Contaminated Water in Finland (Paper presented at 1961 Effluent and Water Treatment Convention, London, Oct-Nov. 1961), Eff. and Wat. Treat. Jour., 1, 171, Oct. 1961.

218. Anonymous, Continuous Control of Effluent Waters, LaTechnique de l'Eau, 15, p. 50, Dec. 1961.

219. Schmidt and Marlies, Polymer Theory and Practice.

220. Terry, L.L., Let's Stop Poisoning Our Water, This Week Mag., Dec. 3, 1961, pp. 12, 14, 17.

221. U.S.P. 2,937,143: Flocculating and Settling of Slimes in Water.

222. Larios, C.J., Town Filters Hudson River Water after Drought Proves Its Safety, Wat. Works Engng., Nov., 1961.

223. Ettinger, M.V., and Middleton, F.M., Plant Facilities and Human Factors in Taste and Odor Control Taste and Odor Control, Journal of Ind. Chem., Sales Div. of W. Va. Pulp and Paper Co., 22, Nov. 1956.

224. Middleton, F.M., et al., Fundamental Studies of Taste and Odor in Water Supplies (Paper Presented at joint meeting of W. Va. Section and W. Va. Sewage and Ind. Wastes Assn., Oct. 1951), JAWWA, June 1952.

225. Heukelekian, H., and Balmat, J.L., Chemical Composition of the Particulate Fractions of Domestic Sewage, SIW (1959), 31, 413-423. WPA, 32, 344-345, Oct. 1959.

226. Liubimov, V.I., and Kagan, Z.S., The Dynamics of Volatile Organic Acids formed During the Anaerobic Decomposition of Organic Compounds by Micro-Organisms in Methane Tanks, Microbiology, Moscow, 1958, 27, 476. JWPCF 1960, 32, 110. WPA 1447, 33, 274, Aug. 1960

227. Anonymous, Composition of A Domestic Sewage Biochem. Microbiol Technol. Engng., 1, 143-162, 1959. WPA, 33, 94, March 1960.

228. Middleton, F.M., and Lichtenberg, J.J., Measurements of Organic Contaminants in the Nations Rivers, Ind. Engng. Chem., 52, 99A, 1960.

229. Mueller, H.F., et al., Chromatographic Separation and Identification of Organic Acids-Application to Detection of Organic Acids in River Waters, Anal. Chem., 32, 687, 1960.

APPENDIX A:

U.S. Patent 2,393,269

GPO 812-253-7

Patented Jan. 22, 1946 2,393,269

UNITED STATES PATENT OFFICE

2,393,269

COAGULANT COMPOSITION FOR REMOVAL OF SUSPENDED OR DISSOLVED MATERIALS FROM LIQUIDS

Willem Rudolfs, Piscataway Township, Middlesex County, and Harry W. Gehm, Metuchen, N. J., assignors to The Permutit Company, New York, N. Y., a corporation of Delaware

No Drawing. Application October 2, 1941, Serial No. 413,298

7 Claims. (Cl. 252—181)

This invention relates to the treatment of liquids such as sewage, trade wastes and similar aqueous liquids containing colloidal, suspended or dissolved matter which should be at least partially separated from the liquids. The invention relates more particularly to a new coagulant for treating such liquids, to the method of making the coagulant, and to methods of treating liquids therewith.

Metallic salts such as alum and ferric chloride have been used to coagulate and settle or render filterable the suspended matter in various liquids. In fact, ferric chloride is used extensively with sewage for this purpose, even though it is fairly expensive and objectionable because of its corrosiveness and for other reasons.

We have found that coagulating salts of the multivalent metals such as the chlorides of iron, aluminum, zinc, tin, titanium, chromium, manganese and copper when used in conjunction with various proteinous materials such as gelatine, glue or the like, are very effective coagulants. Such a combination produces equivalent clarification at lower cost compared with ferric chloride alone, or better results may be obtained at equal cost.

Although separate solutions of the metallic salt and proteinous material may be fed to the liquid to be treated, we have found that these ingredients may be used advantageously in a combined form. In general we have found that similar compound formation does not take place with other metal salts, e. g., sulfates or carbonates. Furthermore in such cases the mixtures of the metal salts with the protein materials still show some advantage over the use of the metal salts alone, but this advantage is not as great as that obtained by the use of the protein material metal chloride compounds.

For example, ferric chloride and gelatine may be combined to give a composition of matter in which the gelatine and ferric chloride apparently are chemically combined and which is highly effective as a coagulant and is very convenient for storage, transportation and use.

The quantity of ferric chloride required in this combination for the clarification of liquids such as sewage is substantially smaller than the quantity of ferric chloride that would be required when used alone, and a very rapid and effective formation and settling of floc is obtained. Also, a higher degree of clarification can be obtained with such a combination than is obtainable with economically practical dosages of straight ferric chloride.

Various proteinous materials such as glue, zein, gluten, casein and albumen may be substituted for the gelatine but we have found gelatine of commercial grade (not refined for use as food) to be most satisfactory from the standpoint of cost and efficiency. Some of the other proteinous materials, which generally must be used in their impure forms on account of cost, tend to clarify liquids imperfectly and/or contain inactive ingredients which dissolve in the liquid and contribute to its impurity. Glue, for instance, apparently contains protein degradation products which dissolve in the liquid, and is generally less efficient as a purifying agent in combination with the ferric chloride than is gelatine although it is generally second best of the available proteinous materials. It will be appreciated that such proteinous materials as are capable of use in combination with ferric chloride, in their impure or crude forms which are available for use in treating sewage and industrial wastes, vary widely in composition and such considerations may determine the particular proteinous material to be used in the clarification of a particular liquid at a particular time and place. Such other proteinous materials apparently owe their utility to their content of protein which is identical with or similar to that of gelatine.

Due to the wide variations in proteinous materials, including gelatine, available for use, and to the wide variations in the character of liquids requiring clarification, it is impossible to state a concise rule as to the best ratio of metallic salt to proteinous material and the best quantity of the composition to use for treating all liquids. The following disclosure is to be read and understood in the light of this situation. Those skilled in the arts of liquid clarification and sewage treatment appreciate the extreme variations encountered in practice and demand a highly flexible means for meeting special conditions. The following disclosure will not therefore be regarded by those skilled in the art as being lacking in specific and critical data.

Coagulants comprising a metallic salt such as ferric chloride in combination with a proteinous material may be prepared in various ways. For example, a suitable compound may be prepared by grinding together about 1 to 7 parts of dry gelatine and 5 parts of anhydrous ferric chloride with just sufficient water so that the compound can be kneaded to a uniform paste. The paste can be stored as such, evaporated to produce a dry product, or diluted with water to form a stable liquid product. A dilution such that one gallon of solution contains 0.25 lb. of iron is satisfactory.

A suitable compound or composition may also be prepared by simply mixing gelatine and ferric chloride in the presence of water. Solutions of ferric chloride and gelatine may be simply mixed to produce a solution of the composition ready for use. The concentrations of the solutions are not critical but we prefer substantially saturated solutions. Dilute solutions are inconvenient for storage and shipment, and highly dilute solutions are not stable in storage.

Compositions prepared by simply mixing solutions of the gelatine and ferric chloride may be concentrated by evaporation and even reduced to dryness but for the production of a dry composition we prefer to grind the gelatine and anhydrous ferric chloride together in the presence of only sufficient water to moisten the mixture. The product may be dried in the air or by the application of heat and powdered or flaked for convenience in handling and ready solubility. When the gelatine and ferric chloride are ground together heat is evolved and a solution of the product in water exhibits freezing points and vapor pressure changes, pH characteristics, speed of solubility, and other characteristics, all of which indicate that the ferric chloride and gelatine have entered into chemical combination. In fact, the ferric chloride is less corrosive in this combination and cannot be separated by washing out of the product with cold water as it could be if it were simply mixed and not combined with the proteinous material.

As stated above, the proportions in which the proteinous material and metallic salt may be combined vary within a wide range. Gelatine has been found to be effective when combined with ferric chloride in proportions as low as 1 part by weight of dry gelatine to 5 parts by weight of anhydrous ferric chloride and possibly even a smaller proportion of gelatine may be effective under some circumstances. Ordinarily, however, the ratio of gelatine to ferric chloride should not be less than 1 to 3 and the customary range is 1 part of gelatine to from 1 to 2 parts of ferric chloride. On the other hand, it is not considered practical or economical to combine more than about 4 parts of gelatine with 3 parts of ferric chloride. The best proportions for gelatine and ferric chloride appear to be 2 parts gelatine to 3 parts ferric chloride. This combination is definitely superior with respect to stability, lack of corrosiveness, solubility in water, and ability to dry well and remain as a dry product without taking up water.

In general, the proteinous material, when combined with ferric chloride, should be combined in the proportion of about 1 to 7 parts of the former for each 5 parts of the latter, by weight. With other metallic salts than ferric chloride, the proportion of proteinous material to be added is increased or decreased so that the time required for the appearance of the first visible floc is approximately the same as that obtained with the foregoing proportions of proteinous material to ferric chloride.

Under some circumstances when adding the proteinous material-metallic salt combination to liquids, it is found advantageous to dilute a concentrated solution of the compound with ferric chloride or similar salt solution instead of with water. When this is done, we ordinarily use a compound containing a ratio of proteinous material to ferric chloride of 2 to 3, but the ratio in the diluted solution does not fall below 1 to 5. Even at this low ratio, the proteinous material combined with the ferric chloride or similar salt materially aids the flocculation of suspended solids.

Another example of a method of making a good coagulant is as follows. Dissolve gelatine in hot water, say 3 parts by weight of gelatine to 20 parts of water and then add the ferric chloride, say 2 parts. The mixture quickly stiffens and kneading is necessary to complete the reaction. The resulting pasty compound may be stored and shipped as such or dissolved in water or dried, preferably in the form of flakes. The dry product, the paste and even concentrated solutions are quite stable, non-hygroscopic and relatively non-corrosive. This solution if diluted to such a degree that one gallon of the liquor contains ¼ lb. of iron will remain stable indefinitely. If the composition is diluted to such an extent that 1 gallon contains 1/10 lb. of iron, it will remain stable for about two weeks. Higher dilutions will change in color from dark brown to yellow within about 24 hours and such solutions lose, to a large extent, their coagulating properties. Such highly diluted solutions are however stable for a few hours, say up to 10 hours, and the instability of the dilute solutions prepared for immediate use does not introduce a troublesome factor.

The coagulants of our invention may be applied to liquids to be clarified in the usual manner as will be understood by those skilled in the art. The coagulant ingredients may be fed separately or combined in solution form, or the compound may be fed in solid form. Usually, dilute solutions of the coagulant are easier to handle and can be fed in more accurate proportions to the liquid to be clarified. Some agitation of the liquid after addition of the coagulant is usually desirable since the floc settles very rapidly.

The clarification process and coagulants of our invention are particularly effective for the treatment of sewage and industrial wastes, but may also be used for general water coagulation processes. In some cases, however, it may be desirable to feed turbidity, i. e., clay or similar material, along with the coagulant or coagulant ingredients into the liquid to be treated in order to obtain the best results.

The proportion of coagulant required will vary with the liquid to be treated, the degree of treatment required, the composition of the coagulant, and many other factors. For treating average domestic sewage (approximately 200 P. P. M. total suspended solids and 200 P. P. M. B. O. D.) a suitable solution may be fed to provide in the sewage 4 to 8 parts of gelatine and 20 to 60 parts of ferric chloride per million. With more dilute sewages, lower concentrations may be used. In general, the proteinous material-metallic salt compound can be used with good results to provide only about 50 to 80% as much metal as would be required if the metallic salt were used alone.

Ordinarily in sewage treatment, the ferric chloride-gelatine combination works better at pH values below 7 than at pH values above 7. Its effectiveness increases with decreasing pH values within the range from about 8.0 down to pH 2.5. Above pH 8 the floc particles formed are smaller than at lower pH values and at a pH value of 11 the clarification of the sewage is definitely imperfect.

Perhaps the most important characteristic of the action of the metallic salt-proteinous material combination when operating conditions are normal is the character of the floc formed and its speed of formation. When the proteinous material and metallic salt are used jointly, observation indicates that the time required for the appearance of the first visible floc (under specified conditions of lighting, etc.) is substantially increased as compared with the time required for such floc appearance when the metallic salt is used alone. This makes it possible for the coagulating chemicals to be more thoroughly dispersed throughout the liquid before the actual

clumping together of the small floc particles into larger floc aggregates takes place. Thus the smaller floc particles have a better opportunity to come in contact with the suspended and dissolved matter to be removed before the actual formation of the floc aggregates takes place. But the total time period for the formation of the first visible floc is extremely small compared with the time required for the entire coagulation process which may be said to include three stages, viz.: (*a*) formation of first visible floc, (*b*) clumping together of small floc particles into larger aggregates, and (*c*) settling of these floc aggregates with the occluded suspended and dissolved matter. However, once the floc has started to form, the clumping together into the larger aggregates proceeds more rapidly than in the case of the straight metallic salt and also the aggregates so formed are larger, more stable and tougher, so that they do not break up on being disturbed and even when broken up by violent stirring or pumping, reform and settle.

Sewage which has been properly treated with the composition has about the same B. O. D. and oxygen consumed values as sewage which has been properly treated with ferric chloride alone. This proves that the added proteinous material is removed with the floc and does not remain in the clarified effluent for, if it remained, these values would be higher.

The sludge formed maintains its flocculated form even after decomposition sets in and resists redispersion. Of the various proteinous materials, gelatine gives the largest reduction in the ferric chloride requirements for complete clarification of a sewage. Some other proteinous materials, however, give a large floc but impurities or non-proteinous materials present tend to dissolve in the sewage effluent and increase the oxygen demand. Others are satisfactory except for the fact that they fail to reduce appreciably the amount of ferric iron required for clarification over that necessary when $FeCl_3$ alone is employed.

Results similar to those obtained by the use of the described proteinous material-metallic salt combination may be obtained by proper use of proteinous material and metallic salt introduced separately into the liquor to be treated. For example, gelatine may be first added and thoroughly distributed and ferric chloride may then be added and quickly and thoroughly distributed. If the metallic salt is added before adding the proteinous material, e. g. about 1 minute earlier, the advantages of the combination are lost, and if the ingredients are added simultaneously, some advantage is obtained but the results are not as good as are obtained by using the proteinous material-metallic salt compound or by adding the proteinous material before the metallic salt. Even when the proteinous material is fed to the liquid before the metallic salt, however, it is necessary to control the ratio of proteinous material to metallic salt and this problem is eliminated by the use of the compound of the two ingredients.

The metallic salt-proteinous material combinations of our invention may be used, like ferric chloride and other coagulants, with additions of lime and other treating agents. Gelatine, whether added separately or in combination with ferric chloride, reduces the ferric chloride requirements but use of the combination definitely avoids the possibility of substantial quantities of the gelatine escaping flocculation and remaining the liquid effluent.

Sludge produced by the combination is more stable, remains amenable to dewatering longer and loses its dewatering characteristics more slowly than a ferric chloride sludge which, if allowed to stand too long, becomes gelatinous and must be treated, e. g., with lime and ferric chloride to restore its dewatering properties. The ferric chloride-gelatine sludge filters well and yields a firm non-gelatinous cake containing less water than a ferric chloride sludge. The proportions stated in the claims are in terms of parts by weight.

The terms and expressions which we have employed are used as terms of description and not of limitation, and we have no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but recognize that various modifications are possible within the scope of the invention claimed.

We claim:

1. A coagulant for use in removing dissolved or suspended matter from liquids comprising ferric chloride and gelatine combined in the proportion of about 1 to 7 parts by weight of gelatine to 5 parts by weight of ferric chloride.

2. A coagulant for use in removing dissolved or suspended matter from liquids comprising about 1 to 2 parts by weight of a chloride of a trivalent metal combined with 1 part by weight of an albuminous protein.

3. A coagulant composition for use in removing dissolved or suspended matter from liquids comprising a compound of 5 parts by weight of a chloride of a trivalent metal chemically combined with about 1 to 7 parts by weight of an albuminous protein, said compound being dissolved in a dilute solution of hydrochloric acid.

4. A coagulant composition for use in removing dissolved or suspended matter from liquids comprising a compound of 5 parts by weight of a chloride of a trivalent metal chemically combined with about 1 to 7 parts by weight of gelatine, said compound being dissolved in a dilute solution of said salt.

5. A method of preparing a coagulant for use in removing dissolved or suspended matter from liquids comprising mixing in the presence of sufficient water to form a thick paste about 1 to 7 parts by weight of an albuminous protein with about 5 parts by weight of a chloride of a trivalent metal.

6. A method of preparing a coagulant for use in removing dissolved or suspended matter from liquids comprising grinding together 1 to 7 parts by weight of solid gelatine and 5 parts by weight of ferric chloride together with just sufficient water to form a pasty mass.

7. A method of making a coagulant for use in removing dissolved or suspended matter from liquids comprising dissolving about 3 parts by weight of gelatine in about 20 parts by weight of water, adding about 2 parts by weight of ferric chloride to the solution, and kneading the resulting pasty mass.

WILLEM RUDOLFS.
HARRY W. GEHM.

GPO 812-253-8